PB-217 254

SORPTION AND MOVEMENT OF POLLUTED WATER IN SOIL

J. W. Biggar, et al

Public Health Service
Washington, D. C.

1973

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

WP-0081-06-07

Cinn

PB 217 254

Sorption and Movement of Polluted Water in Soil

U.S. Public Health Service
Grant WP0081-06-07

J.W. Biggar
R.L. Riggs

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 2215

LIBRARY
FWPCA, Ohio Basin Region
[illegible] University Pkwy. Cinci, O. 45226

291

Appendices

Sorption and Movement of Polluted Water in Soil

U.S. Public Health Service
Grant WP00081-06-07

J. W. Biggar
R. L. Riggs

1a

Appendix I

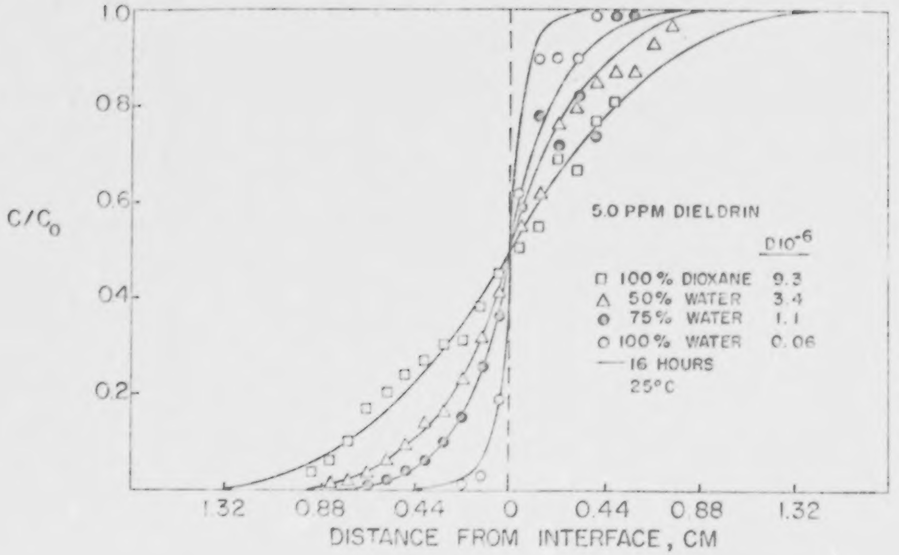
I. Apparent self diffusion coefficients of dieldrin in sodium saturated kaolinite.

The movement of slightly soluble chlorinated hydrocarbons such as dieldrin through porous materials such as soil saturated with water appears to be controlled by the solubility of the material in water. Of the two transport mechanisms, mass flow of water and molecular diffusion, the latter is probably the most significant. Consequently the supply of the organic chemical in the solution phase will be controlled by the solubility and whatever mixing and or movement that may occur is probably dependent upon diffusion.

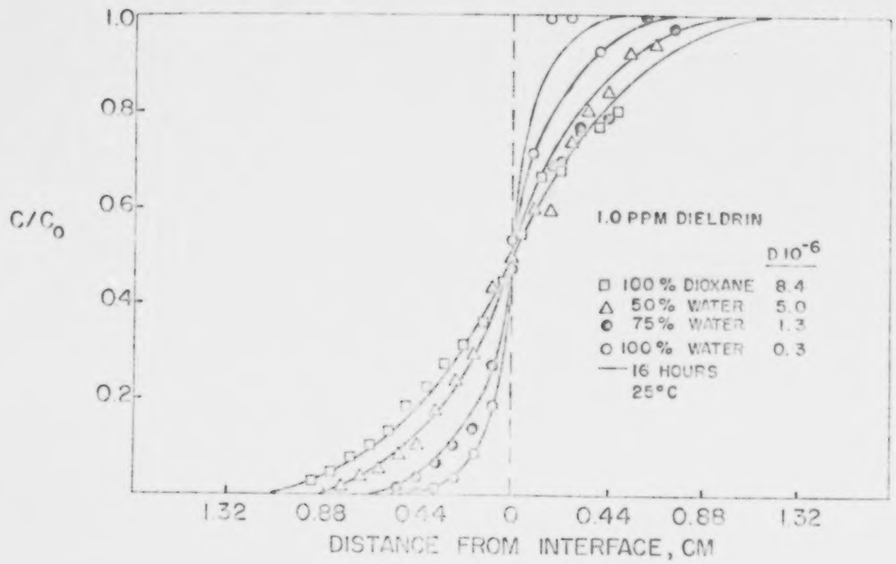
If an additional factor is introduced into the system in the form of a solubilizing agent then both the movement and the diffusion will be enhanced by 10- to 100-fold.

Diffusion coefficients and adsorption processes are dependent upon the temperature of the system. Generally the diffusion coefficients increase and the amount of adsorbate adsorbed decreases with temperature. For a given concentration of added organic constituent both the diffusion coefficient and reduced adsorption should contribute to an increase in movement with temperature. Not unrelated however is the increase in solubility of the organic constituent with temperature which may be more significant than the other two.

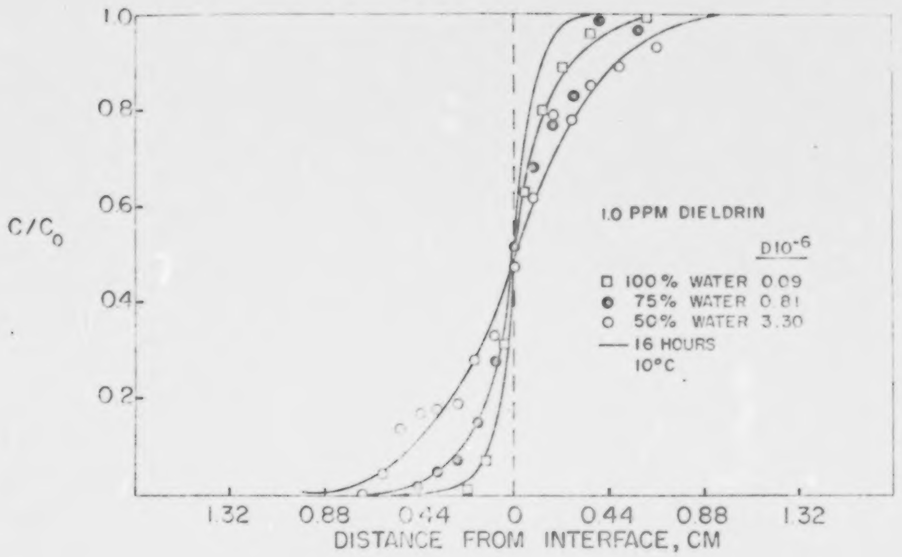
The accompanying graphs in this appendix summarized for 1.0 ppm added concentration of dieldrin in the table of the report serve to bear out the importance of the factors mentioned.



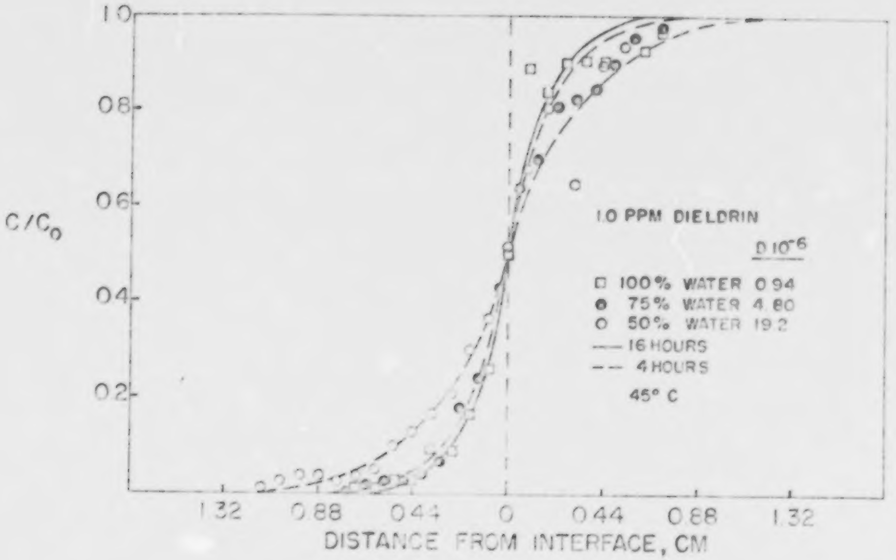
EXPERIMENTAL AND THEORETICAL DISTRIBUTION OF DIELDRIN (C^{14} DIELDRIN VS DIELDRIN) IN Na-KAOLINITE CLAY



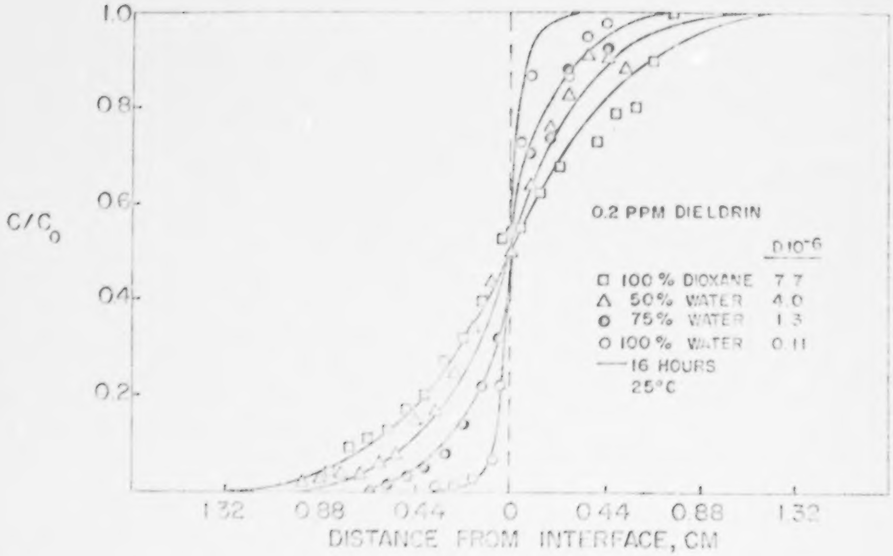
EXPERIMENTAL AND THEORETICAL DISTRIBUTION OF DIELDRIN (C^{14}DIELDRIN VS DIELDRIN) IN Na-KAOLINITE CLAY



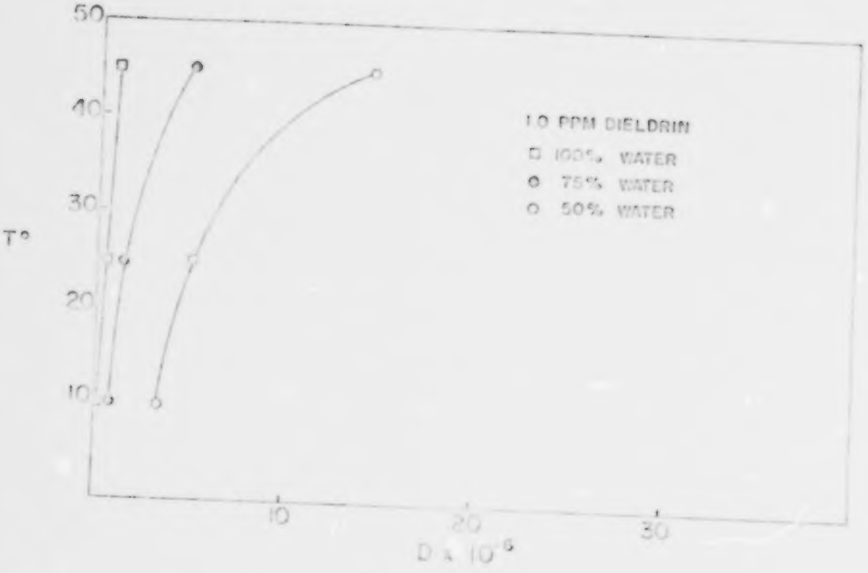
EXPERIMENTAL AND THEORETICAL DISTRIBUTION OF DIELDRIN (C^{14} DIELDRIN VS DIELDRIN) IN Na-KAOLINITE CLAY



EXPERIMENTAL AND THEORETICAL DISTRIBUTION OF DIELDRIN (C^{14} DIELDRIN VS DIELDRIN) IN Na-KAOLINITE CLAY



EXPERIMENTAL AND THEORETICAL DISTRIBUTION OF DIELDRIN (C^{14} DIELDRIN VS DIELDRIN) IN Na-KAOLINITE CLAY



VARIATION OF D WITH TEMPERATURE FOR DIELDRIN IN Na-KAOLINTE CLAY

Appendix II

II. Desorption isotherms and recovery of dieldrin and DDT.

In addition to examining the adsorption properties of various chlorinated hydrocarbons, some of our results indicate for some materials the desorption may differ significantly from adsorption. Both are important to the changes of pesticide in the field but usually the desorption problem is given less attention theoretically when qualitatively assessing the tendency of the pesticide to move. From a practical viewpoint the normal wetting and drying process common to field conditions should also be evaluated. A laboratory experiment performed in conjunction with desorption experiments on dieldrin to compare in the soil extraction methods is described for two soils and two common extraction procedures.

From an analytical point of view, two main problems are at once evident in the determination of soil pesticide residues. The first obstacle is obtaining a representative soil sample. Pesticide applications are not uniform, and variations in soil type in a field or profile may necessitate the modification of extraction procedures. Lykken (1963) has extensively discussed the problems associated with soil sampling.

Soil samples vary widely in moisture content and per cent organic matter. It is customary for residue data to be reported on an air-dry basis. Oven drying of soil samples to constant weight risks the loss of pesticides, even chlorinated hydrocarbons, due to volatilization, co-distillation and thermal decomposition. High organic matter content in soils usually results in inefficient residue recoveries and an increase in interferences which must be removed by extensive cleanup procedures or circumvented by means of specific detection systems.

The second problem is to determine what extraction technique is most efficient for the particular type of soil and residue(s) involved. Very few extraction techniques for soil residues are noted in the literature. Shell Development Co. (1964), Burchfield and Johnson (1965) and Teasley and Cox (1966) account for the most commonly used general soil extraction procedures. Extraction efficiency is usually checked by spiking a sample with a known amount of pesticide before extraction. It can be argued that this is not a true measure of the extraction procedure, for the added standard has not undergone the field conditions of the sample, and may not be as strongly adsorbed to the soil or as closely associated with its organic matter.

The objectives of this work are to compare the efficiencies of commonly used soil extraction techniques for the recovery of D.D.T. and dieldrin, and to subsequently use these methods to determine the effects that long term contact and weathering might have upon the recovery of these pesticides.

Experimental

Dieldrin and p,p'-DDT were obtained as 99% pure and were used without further purification. Carbon-14 labeled dieldrin (99% pure, 1.45 mc/mm) and p,p'-DDT (99% pure, 4.93 mc/mm) were obtained from Nuclear-Chicago Corp. All organic solvents were nanograde reagents and were further distilled from glass. Preactivated 60/100 mesh Florisil adsorbent was used in column cleanup of the extracts.

Residues were determined by gas chromatography, utilising electron capture and microcoulometric titration detectors. The electron capture unit was a Varian Aerograph 600-D gas chromatograph equipped with a 250 mc tritium foil detector. A 5% SE-30 packing on 60/80 mesh Chromosorb W support in a 5' x 1/8" pyrex column was used. Column temperature was 180°C, gas flow was high purity N_2 at 80 ml/min.

The Dohrmann C-200 microcoulometer was equipped with a T-300S titration cell. The 4' x 1/4" pyrex column was packed with 5% DC-200 on 80/100 mesh Aeropak 30. Temperature and flow parameters were maintained as above.

The carbon-14 labeled pesticides were counted in a Packard Tri-Carb model 314E liquid scintillation spectrometer. Some samples were also analyzed using a Nuclear-Chicago model 4998 gas radiochromatography system.

The soils used were Hanford sandy loam and Panoche clay loam. These soils are typical agricultural soils from California's San Joaquin Valley. Their properties are listed in Table II.

Table II.

Properties of the Experimental Soils.

soil	% sand	% silt	% clay	% organic matter	surface area in m^2/gm total	external
Hanford	52.7	35.2	41.9	1.80	24.6	13.5
Panoche	35.2	22.9	41.9	2.10	127.3	56.6

Kilogram lots of air-dry soil were screened through a 2mm sieve and thoroughly mixed. The soils were uniformly coated with DDT or dieldrin by adding soil to a rotary evaporator flask containing an aqueous emulsion of the pesticide. The pesticide emulsions were made up from 20% pure pesticide, 76% toluene and 4% Triton X-100 to simulate commercial formulations. Adequate aliquots of these concentrates were added to excess water, to yield final soil pesticide concentrations of 0.50, 1.00 and 2.00 ppm. The soil was added and the slurry mixed, then placed in 10" x 10" x 2" pans and allowed to air-dry at 25°C.

To simulate weathoring, enough water was added to the air-dry soils to form a saturated paste. The slurry was then thoroughly mixed and allowed to air dry again. This wetting-drying cycle was repeated 15 times over a period of 48 weeks, with samples being withdrawn initially and after 5, 10 and 15 applications of water. The soils were reduced to fine powder and well mixed before 50 gm were sampled for analysis.

Some of the soil samples were spiked at this point with known amounts of C^{14} labeled pesticides to determine the efficiency of the extraction and cleanup processes.

The first extraction procedure is a modification of the Shell Development Co. method (1964). A 50 gm representative sample is weighed into a 500 ml Erlenmeyer flask, and just enough distilled water added to make a slurry. One hundred ml of hexane:isopropanol (3:1) is added and the sample vigorously shaken for 20 minutes on a wrist action shaker. Decant and retain the hexane phase in a seperatory funnel. The extraction is repeated twice more and the hexane phases combined. Isopropanol is washed from the hexane with water and the hexane extract dried over anhydrous Na_2SO_4. The sodium sulfate is filtered off and the hexane phase is concentrated to 5 ml or less using a 500 ml Kuderna-Danish evaporative concentrator.

The second procedure employs the Soxhlet extractor. A 50 gm sample is weighed into an extraction thimble. The receiving flask is charged with 125 ml of hexane:acetone (9:1). The sample is extracted for 16 hr in the manner of Teasley and Cox (1966), after which the solvent is transferred to a Kuderna-Danish evaporator and concentrated to 5 ml or less.

Although the soils used were relatively free of interfering materials, many soil samples are not. Therefore the extracts were taken through a standard column cleanup procedure (Mills, 1961) to simulate recovery from interfering substances. The concentrated extracts were transferred to a 4-inch column of Florisil topped with one-half inch anhydrous Na_2SO_4 and prewetted with petroleum ether. The column was percolated with 250 ml each of diethyl ether:petroleum ether (6:94) and (15:85) respectively. DDT elutes with the first 250 ml, dieldrin with the remainder. The eluate fractions were evaporated just to dryness and taken up in 1.00 ml of benzene. Aliquots were taken for gas chromatographic or liquid scintillation analysis and the DDT or dieldrin in the fractions was determined.

Discussion

The mean recoveries of the pesticide residues, corrected for extraction efficiency, are presented in Figures 1-4. The mean recovery is shown for the 3 experimental concentrations in 2 soils as determined by 2 quite different extraction procedures. The 95% confidence interval of the mean is also presented and was determined by:

$$\bar{X} \pm t0.05\ s_{\bar{X}}$$

$\bar{X}$ being the mean recovery of three replicate samples, t is the deviation of the estimated mean and $s_{\bar{X}}$ is the standard error of the mean. The

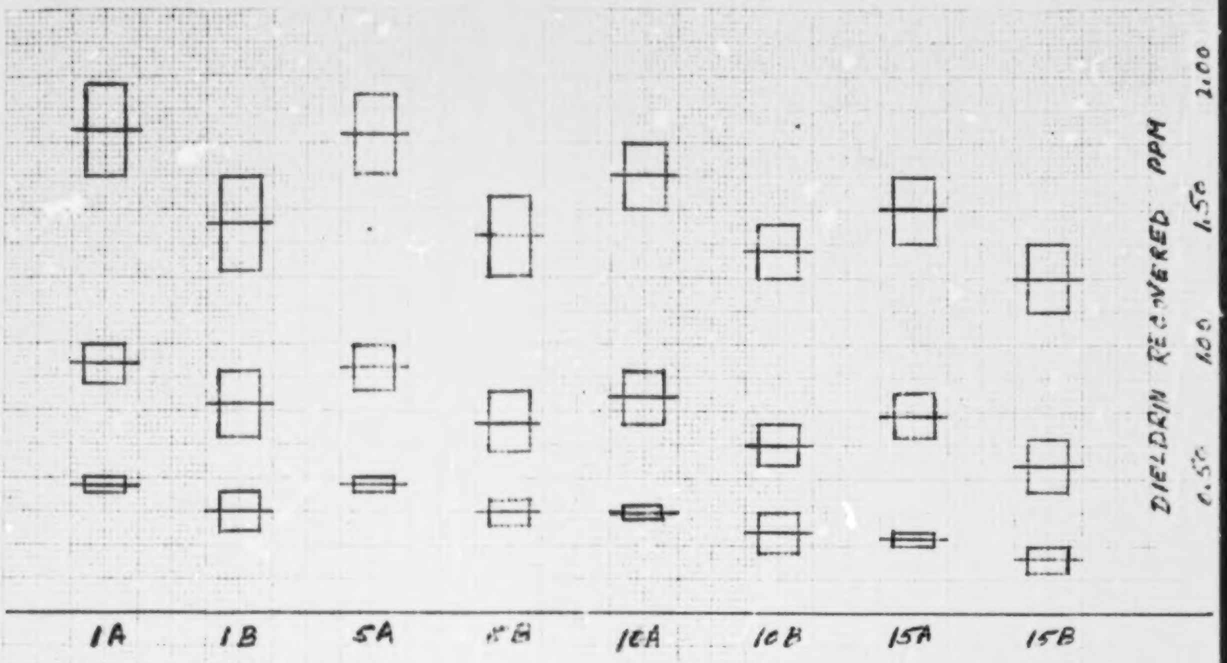
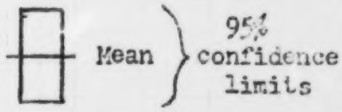


Figure 1: Recovery of Dieldrin from Hanford sandy loam.

number indicates wetting-drying cycle
A = Sohxlet extraction
B = Shell method


Mean
95% confidence limits

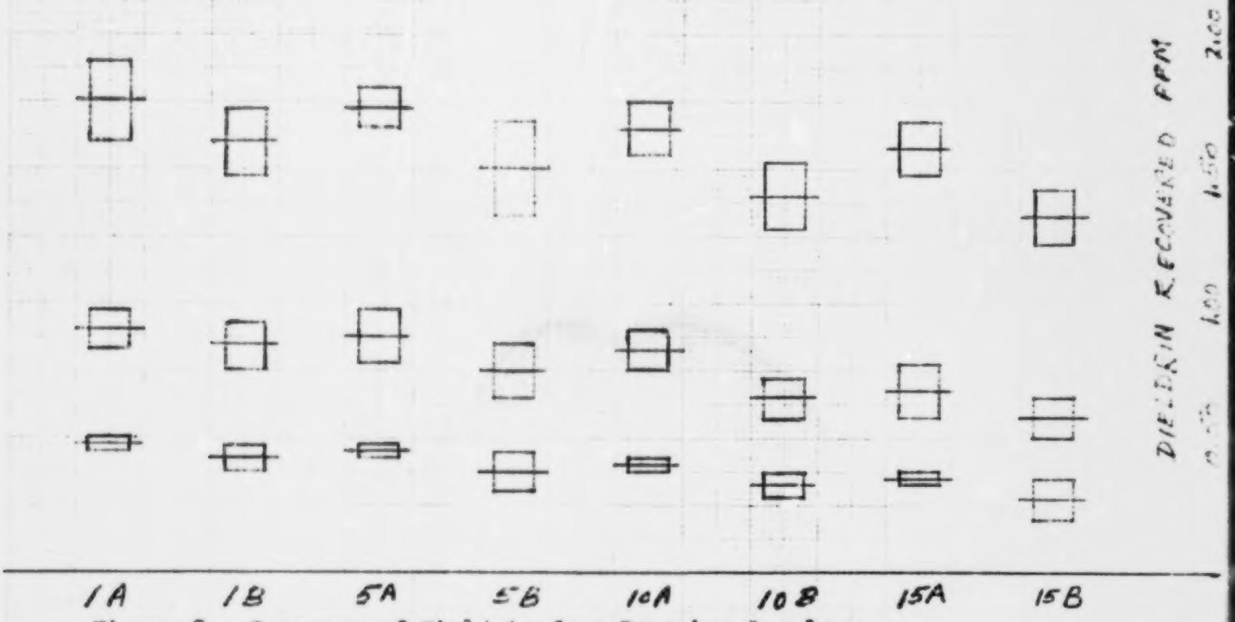
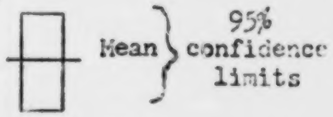


Figure 2: Recovery of Dieldrin from Panoche clay loam.

number indicates wetting-drying cycle
A = Sohxlet extraction
B = Shell method


Mean
95% confidence limits

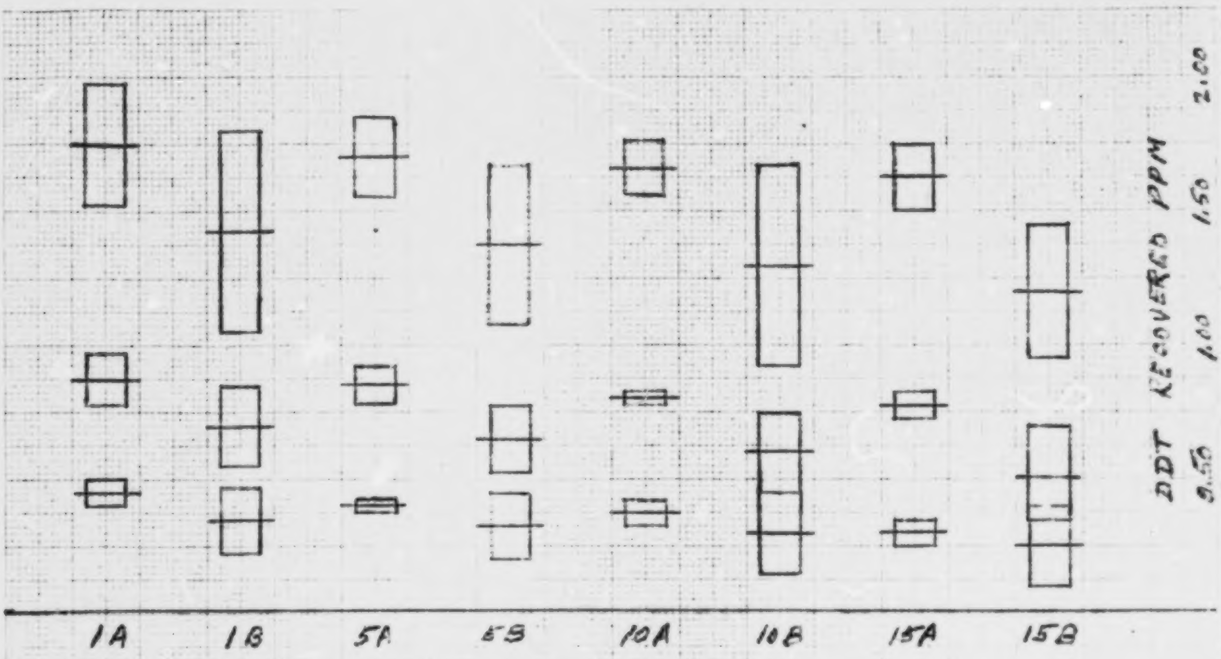


Figure 3: Recovery of DDT from Hanford sandy loam.

number indicates wetting-drying cycle
A = Sohxlet extraction
B = Shell method

Mean } 95% confidence limits

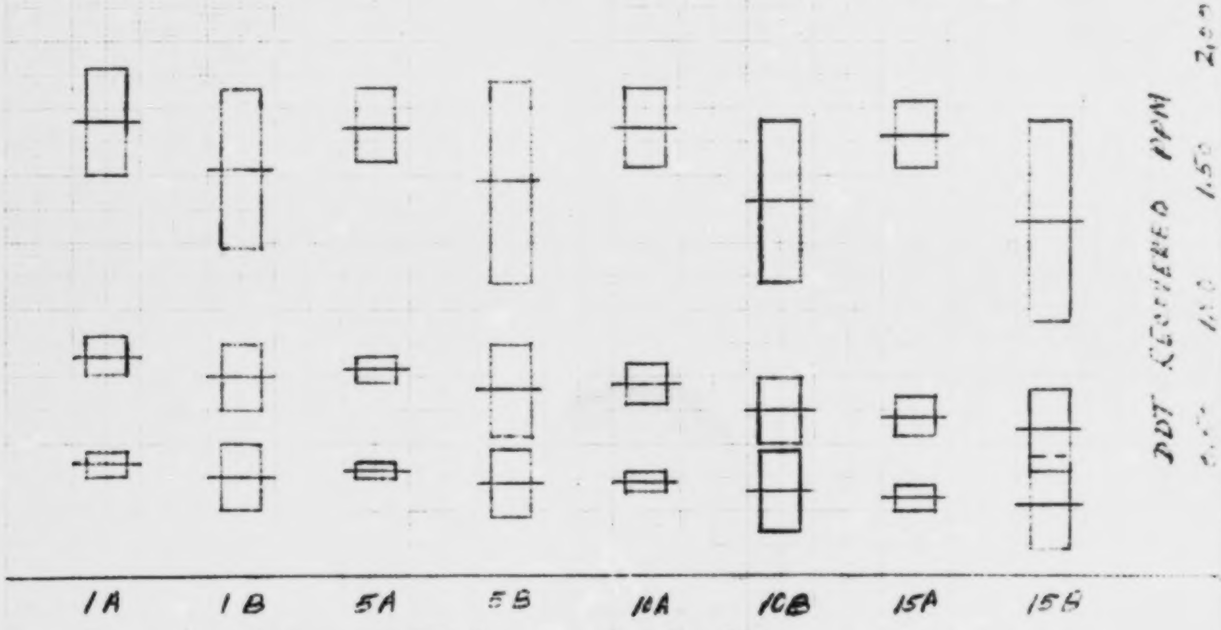


Figure 4: Recovery of DDT from Panoche clay loam.

number indicates wetting-drying cycle
A = Sohxlet extraction
B = Shell method

Mean } 95% confidence limits

relative size of the confidence interval indicates the precision of the method. The overall precision of dieldrin recovery was comparable for both extraction methods at all concentrations in both soils. However, the Shell method gave consistently lower recoveries. Both extraction techniques became less efficient as the amount of dieldrin in the soil increased. The differences in mean recoveries between the Shell and Sohxlet extractions are statistically significant for all three sample concentrations. Generally speaking, dieldrin recoveries were greater than the amounts of DDT extracted from both Hanford and Panoche soils. Dieldrin recovery (Sohxlet) from Hanford was initially greater than from Panoche, but after 15 wetting cycles more was recovered from Panoche than Hanford. The Shell method gave better results with Panoche than it did for Hanford, but was inferior to the Sohxlet method for both soils.

The precision of DDT recovery was comparable at all concentrations for both soils when the Sohxlet technique was used. The differences in mean recoveries between the Sohxlet and Shell methods are statistically significant, the Sohxlet technique giving consistently better results. The Shell method for DDT is not precise because of the extent of the confidence limits at higher concentrations and overlap of the limits at low concentrations. DDT recoveries (Sohxlet) were consistently better from Hanford than from Panoche. The Shell procedure extracted more DDT from Panoche than from Hanford.

It should be noted that since extraction efficiency becomes less as residue concentrations increase, the spiking of samples does not necessarily accurately reflect recovery from field samples. It is also obvious that a combination of weathering and tillage reduces the availability of a pesticide for extraction. Volatilization and co-distillation could account for some residue loss, but this amount is slight when compared to the changes noted here. No decomposition products were detected with the exception of trace amounts of p,p'-DDD in the final DDT analyses.

Literature Cited

Burchfield, H. P., and Johnson, D. E., "Guide to Analysis of Pesticide Residues," U.S. Public Health Service, Dept. of Health, Education, and Welfare, Washington, D. C. (1965).

Lykken, L., Residue Rev. 3, 19 (1963).

Mills, P. A., J. Assoc. Offic. Agr. Chemists 44, 171 (1961).

Shell Development Co., Agricultural Research Div., Method MMS-43/64, Modesto, Calif. (1964).

Teasley, J. I., and Cox, W. S., J. Agr. Food Chem. 14, 319 (1966).

Appendix III

III. The adsorption of the Gamma- and Beta-Isomers of 1,2,3,4,5,6-Hexachlorocyclohexane on Soils.

Acknowledgement: The authors, A. C. Mills and J. W. Biggar, wish to gratefully acknowledge the support of Grant WP-00081-06 which made possible the comprehensive study reported in the accompanying thesis.

It is a known fact that the behavior of a chemical in a solvent embodied in a porous material is determined by the physical and chemical properties of the chemical itself as well as those of the solvent and the surfaces of the porous material. Many of these same properties may control to some extent the stability of the compound and its resistance to biological decomposition.

The present appendix contains a comprehensive study of the behavior of two isomers of BHC in contact with several adsorbents and involving several solvents. Certain thermodynamic quantities are sought for the isomer adsorption on a limited number of surfaces and mainly water as the solvent.

An abstract immediately following this introduction and a summary at the end provide a condensed version of the accomplishments.

Flow experiments are reported at the conclusion of the thesis.

Andrew Clinton Mills

January, 1967

Soil Science

The Adsorption of the Gamma- and Beta-isomers of 1,2,3,4,5,6-Hexachlorocyclohexane on Soils

Abstract

The adsorptive behavior in solution of γ-BHC(lindane) and its stereoisomer, β-BHC, was studied by means of laboratory equilibrium studies. Analysis was performed both by liquid scintillation counting (L.S.) of the C^{14}-tagged solutions and by electron-capture gas chromatography (G.C.). Following initial adsorption studies involving several adsorbents and four solvents, isotherms were obtained at different temperatures in the range 10 to 40°C. The isotherm studies were carried out on four adsorbents, representing soil components, from aqueous and hexane solutions at low concentration levels.

Decomposition of γ-BHC was observed in hexane and benzene solutions on alumina, $Mg(OH)_2$, and Venado Clay. This was deduced by comparing L.S.- and G.C.-derived solution concentration values and verified by the presence of peaks of the decomposition products on the gas chromatograms.

Adsorption of lindane from solution in general increased according to the following order of solvents: ethanol < benzene < hexane < water. Relatively low adsorption of lindane from hexane and benzene occurred on Staten peaty muck, with the greatest adsorption being on silica gel and Venado clay. The greatest adsorption of lindane from water was on Staten peaty muck, ion exchange resins, and Venado clay.

No positive adsorption from ethanol occurred except to a small extent on Staten peaty muck. The importance of dipole-dipole interactions in lindane adsorption was deduced.

Nearly linear normal isotherms (x/m vs. c) and 'corrected' isotherms (x/m vs. c/c_o) were obtained. Comparing these two types of isotherms one concludes that the effect of temperature on solubility is the only factor tending to make the adsorption process exothermic. With one exception, the relative positions of the aqueous γ-BHC and β-BHC isotherms with respect to the four adsorbents were the same. Linear log-log plots were obtained and the Freundlich constants calculated. The constant $1/n$ increased with temperature according to theory. It is therefore expected that normal isotherms for a given system will intersect while corrected isotherms will diverge. Higher k values (normal isotherms) were obtained for β-BHC adsorption from water relative to γ-BHC. But uniformly lower k' values (corrected isotherms) were obtained for the β-BHC isotherms compared to that of γ-BHC, indicating greater adsorbability of lindane than β-BHC from water at nearly constant fugacities. Maximum surface coverages attained for the aqueous systems in the isotherm studies were very low -- less than 1×10^{-4}.

Values for $\Delta \bar{G}^o$, $\Delta \bar{H}^o$, and $\Delta \bar{S}^o$ of adsorption were determined. $\Delta \bar{G}^o$ values followed the same order as Freundlich k constants. $\Delta \bar{H}^o$ values ranged from +0.7 to -8.4 kcal/mole. The solubility-corrected values for $\Delta \bar{H}^o$ and $\Delta \bar{S}^o$ were also obtained ($\Delta \bar{H}^{o'}$ and $\Delta \bar{S}^{o'}$, respectively). Uniformly positive $\Delta \bar{S}^{o'}$ values indicated more degrees of freedom for BHC molecules in the adsorbed state than in the solid state. Low values for $\Delta \bar{S}^{o'}$ in silica gel-water systems indicated considerable immobilization of molecules adsorbed on this adsorbent.

Isosteric heats (Q_Γ) and heats obtained for a constant change of surface tension ($\Delta\sigma$) were calculated. Unlike isosteric heats, the latter heats, designated as $\Delta \bar{\bar{H}}\sigma$, were shown to represent the true difference at equilibrium between the partial molar enthalpy of the adsorbed solute and that of the solute in solution. The equation for calculating $\Delta \bar{\bar{H}}\sigma$ was derived for dilute solutions obeying Henry's law in solution and on the adsorbent. Values for Q_Γ were of the same order of magnitude as $\Delta \bar{\bar{H}}\sigma$ but the trend with surface coverage sometimes differed. The significance of the change in $\Delta \bar{\bar{H}}\sigma$, and in $\Delta \bar{\bar{S}}\sigma$, with surface coverage is discussed.

Values for the integral free energy of adsorption were calculated. Integral heats of adsorption were calculated for two systems. These increased uniformly as temperature increased from 10° to 40°C.

Some practical implications of the study are discussed.

21a

The Adsorption of the Gamma- and Beta- Isomers of 1,2,3,4,5,6-Hexachlorocyclohexane on Soils

By

ANDREW CLINTON MILLS
B.S. (Pennsylvania State University) 1952
M.S. (University of Missouri) 1954

DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Soil Science

in the

GRADUATE DIVISION

of the

UNIVERSITY OF CALIFORNIA

DAVIS

Approved:

James W. Biggar

Herman F. Bickman

Committee in Charge

Deposited in the University Library.......................................
Date Librarian

ACKNOWLEDGMENTS

The author wishes to express his appreciation to the Federal Water Pollution Control Administration, Department of Interior, for providing a traineeship grant, which enabled this research to be carried out.

Special gratitude is due to Dr. James Biggar, chairman of the thesis committee, for his guidance and helpful advice. The author is grateful to Dr. Lynn Whittig and Dr. Herman Beckman for their help and advice during the conduct of the research.

The author wishes to convey his gratitude to Dr. David Volman and to Dr. Jerome Jurinak for their suggestions and advice with respect to the theoretical section of the thesis.

The author is grateful to Mr. Ralph Riggs for his frequent assistance and instruction in gas chromatographic analysis. Thanks are also due to Mr. Robert Jackson and Miss Ann Quek for giving willing aid in analyses and in supplying other laboratory needs.

I dedicate this thesis to my wife and
children, whose sacrifice and perseverance
have permitted me to initiate and complete
this research.

TABLE OF CONTENTS

Page

INTRODUCTION.. 1

LITERATURE REVIEW...

Lindane in soils.. 3

Adsorption of organic compounds on soils and clays.............. 8

The chemistry of the BHC isomers................................. 13

THEORETICAL CONSIDERATIONS

Nature of adsorption from solution............................... 25

Adsorption isotherms... 29

Thermodynamics of adsorption from solution..................... 38

1. Determination of $\Delta \bar{G}^o$, $\Delta \bar{H}^o$, and $\Delta \bar{S}^o$................. 39

2. The activity coefficient of the solute in the adsorbed phase.. 46

3. The differential heat of adsorption at constant interfacial tension... 46

4. The effect of the solubility-temperature relationship upon changes of thermodynamic properties in adsorption... 53

5. Free energy change involved in the adsorption process.. 58

EXPERIMENTAL DESIGN AND METHODS

Purpose of study.. 61

Materials.. 61

Experimental procedure and methods.............................. 68

1. Preparation of solutions.................................. 69

2. Procedure in equilibrium studies........................ 71

3. Sampling methods... 72

4. Extraction methods... 74

5. Quantitative analysis of equilibrium solutions........ 76

TABLE OF CONTENTS (cont.)

Page

6. Method of calculation 80
7. Determination of solubilities 81

RESULTS AND DISCUSSION

Initial adsorption experiments 87

1. Influence of heat pre-treatment of adsorbents 87
2. The effect of centrifugation of organic solutions 89
3. Direct measurement of adsorption -- 'solid series' 91
4. Influence of adsorbent mass and the solution volume upon adsorption per gram 93
5. The effect upon lindane adsorption of the cation on exchange complex and of H_2O_2-treatment of Venado clay 95
6. Effect of time period in water bath upon concentration of the bulk solution 97

Adsorption of lindane on several adsorbents from four solvents 99

1. Discussion of adsorption affinities of lindane 99
2. Decomposition of lindane in initial studies 109

Isotherm studies of γ-BHC and β-BHC 118

1. Nature of isotherms obtained 123
2. Changes in the standard partial molar thermodynamic properties associated with adsorption 148
3. Determination of surface activity coefficients 160
4. Changes in differential enthalpy and entropy at constant interfacial tension 162
5. Integral free energies and integral heats of adsorption 181

SUMMARY AND CONCLUSIONS 188

PRACTICAL IMPLICATIONS 198

APPENDIX 203

BIBLIOGRAPHY 237

LIST OF FIGURES

Figure No.	Title	Page No.
1	Molecular model of γ-BHC	16
2	Molecular model of β-BHC	16
3	Gas chromatogram -- Saturated aqueous γ-BHC extracted into hexane	83
4	Gas chromatogram -- Saturated aqueous β-BHC extracted into hexane	83
5	Gas chromatogram -- Standard solution of γ-BHC in hexane	85
6	Gas chromatogram -- Standard solution of β-BHC in hexane	85
7	Gas chromatogram -- γ-BHC-$Mg(OH)_2$ systems	112
8	Gas chromatogram -- γ-BHC-Neutral alumina-hexane system	112
9	Gas chromatogram -- γ-BHC-Ca-Venado clay-hexane system	113
10	Decomposition of lindane in aqueous solutions of meta sodium silicate	117
11a	Adsorption of γ-BHC from water	124
11b	Adsorption of γ-BHC from water	125
12a	Adsorption of γ-BHC from water	126
12b	Adsorption of γ-BHC from water	127
13a	Adsorption of β-BHC from water	129
13b	Adsorption of β-BHC from water	130
14a	Adsorption of β-BHC from water	131
14b	Adsorption of β-BHC from water	132
15a	Adsorption of γ-BHC from nanograde hexane	134
15b	Adsorption of γ-BHC in nanograde hexane on Ca-Staten peaty muck	135

LIST OF FIGURES (cont.)

Figure No. Title Page No.

16 Adsorption of γ-BHC from nanograde hexane................136

17a Adsorption of γ-BHC from nanograde hexane -- lowest five points..137

17b Adsorption of γ-BHC from nanograde hexane -- lowest five points..138

18 Decomposition of γ-BHC on Ca-Venado clay in nanograde hexane...139

19 Adsorption of γ-BHC from water (log-log plot)............141

20 Adsorption of γ-BHC from nanograde hexane (log-log plot) -- lowest 5 points...............................142

21 Adsorption of β-BHC from water (log-log plot)............143

22 Variation of $\Delta \bar{S}^o$ with temperature.......................156

23 Variation of γ_2^s with x/m for γ-BHC aqueous systems at 20°C...161

24a Variation of $-A_T\Delta\sigma$ with m_2^s/m_2 for aqueous γ-BHC systems..166

24b Variation of $-A_T\Delta\sigma$ with $(m_2^s/m_2)m_o$ for aqueous γ-BHC systems...167

25a Variation of $-A_T\Delta\sigma$ with m_2^s/m_2 for aqueous γ-BHC systems..168

25b Variation of $-A_T\Delta\sigma$ with $(m_2^s/m_2)m_o$ for aqueous γ-BHC systems...169

26 Variation of $\Delta \bar{H}_\sigma$ (25°C) with a function of surface coverage..170

27 Variation of $\Delta \bar{H}_\sigma$ at three temperatures with a function of surface coverage for two aqueous γ-BHC systems..171

28 Variation of $\Delta \bar{H}$ (15°C) with a function of surface coverage (γ-BHC-Staten peaty muck-hexane system).........172

29 Variation of $\Delta \bar{H}'$ with a function of surface coverage at 25°C...174

LIST OF FIGURES (cont.)

Figure No.	Title	Page No.
30	Possible relationships between $\bar{H}_2^s$ and $\bar{H}_s$ for aqueous β-BHC and γ-BHC for three adsorbents	176
31	Integral heats of adsorption of γ-BHC from aqueous solutions	187
A-1	Langmuir plots of γ-BHC-water systems	223
A-2	Langmuir plots of β-BHC-water systems	224
A-3	Langmuir plots of γ-BHC-hexane system	225
A-4	Extrapolations for γ-BHC-Staten peaty muck-water systems	226
A-5	Extrapolations for γ-BHC-water systems with bentonite and silica gel	227
A-6	Extrapolations for γ-BHC-Staten peaty muck-hexane system	228
A-7	Extrapolations for β-BHC-silica gel-water system	229
A-8	Variation of γ_2^s with x/m for β-BHC aqueous systems at 20°C	230
A-9a	Variation of $-A_T\Delta\sigma$ with m_2^s/m_2 for aqueous β-BHC systems	231
A-9b	Variation of $-A_T\Delta\sigma$ with $(m_2^s/m_2)m_o$ for aqueous β-BHC systems	232
A-10a	Variation of $-A_T\Delta\sigma$ with m_2^s/m_2 for aqueous β-BHC systems	233
A-10b	Variation of $-A_T\Delta\sigma$ with $(m_2^s/m_2)m_o$ for aqueous β-BHC systems	234
A-11a	Variation of $-A_T\Delta\sigma$ with m_2^s/m_2 for the γ-BHC-Staten peaty muck-hexane system	235
A-11b	Variation of $-A_T\Delta\sigma$ with $(m_2^s/m_2)m_o$ for the γ-BHC-Staten peaty muck-hexane system	236

LIST OF TABLES

Table No.	Title	Page No.
1	Melting points and percent composition in crude BHC of the five most common isomers	13
2	Conformations of isomers of BHC	15
3	Thermodynamic properties of solution of BHC isomers at a concentration of one gram per 100 grams of benzene	21
4	Dipole moments of BHC isomers	21
5	Vapor pressures of the BHC isomers	22
6	Solubilities of the β- and γ-isomers at 20°C in grams per 100 grams of solution	23
7	Influence of maximum effective particle size of solute and temperature upon the solubility of γ-BHC in distilled water	24
8	Characteristics of selected adsorbents	67
9	Estimation of the partition coefficient for two β-BHC solutions	75
10	Solubilities of β- and γ-BHC	86
11	Effect of heat pre-treatment of adsorbents upon adsorption of γ-BHC from benzene solutions at 25°C	87
12	Effect of heat pre-treatment of adsorbents upon adsorption from solutions at 20°C	88
13	Comparison of centrifugation versus direct sampling of a hexane solution of γ-BHC at 20°C	90
14	Effect of method of obtaining sample aliquot of benzene solution at 25°C	91
15	Effect of the mass of Venado clay upon the apparent amount adsorbed per gram from benzene solutions at 25°C	92
16	Effect of mass of adsorbents upon adsorption of lindane from nanograde hexane solutions	94
17	Effect of initial solution volume upon the amount adsorbed at 20.0°C	95

LIST OF TABLES (cont.)

Table No.	Title	Page No.
18	Effect of saturating cation and H_2O_2-treatment upon adsorption on Venado clay from an aqueous solution	96
19	Solution concentration as affected by the time period in the bath before sampling	97
20	Adsorption of lindane on several adsorbents at 20°C and the degree of accompanying decomposition	100
21	Adsorption of lindane from 100 µg/ml benzene solution	101
22	Adsorption of lindane from 100 µg/ml nanograde hexane solution	101
23	Adsorption of lindane from 5.0 µg/ml aqueous solution	104
24	Adsorption of lindane from aqueous solutions on Na-glass beads at 24°C	107
25	Polarizability of lindane and solvents	109
26	Decomposition of lindane in benzene and hexane at 20°C	110
27	Decomposition of lindane in aqueous solutions of meta sodium silicate	118
28	Loss of concentration of standard blank aqueous solutions of β-BHC over the course of an adsorption experiment	120
29	Freundlich constants for the isotherms	144
30	Relationship between 1/n values and temperature	145
31	Some maximum surface coverage values in isotherm studies at 20°C	150
32	Values of $\Delta \bar{G}^o$, $\Delta \bar{H}^o$, and $\Delta \bar{S}^o$ associated with adsorption	154
33	Values of $\Delta \bar{H}^{o\prime}$ and $\Delta \bar{S}^{o\prime}$	155
34	Constant interfacial tension heats and entropy changes in adsorption	177

LIST OF TABLES (cont.)

Table No.	Title	Page No.
35	'Corrected' constant interfacial tension heats of adsorption ($\Delta \bar{H}'$) and entropy changes ($\Delta \bar{S}'$)	178
36	Isosteric heats of adsorption (Q_r)	180
37	Integral free energies of adsorption	182-4
38	Integral thermodynamic properties of adsorption for γ-BHC-water systems	186
39	Estimation of the volume of water required to leach the top one-tenth inch layer of soil at 20°C	200
A-1	Values of c and x/m (L.S. analysis)	204-5
A-2	Comparison of equilibrium concentration values by liquid scintillation counting and gas chromatography	206-8
A-3	Tabulation of reduced concentration for isotherm studies	209-10
A-4	Calculation of c_2^s	212
A-5	Determination of $\Delta \bar{G}^o$, $\Delta \bar{H}^o$, and $\Delta \bar{S}^o$ by the method of extrapolating to zero x/m	213
A-6	Surface activity coefficients (γ_2^s)	214-6
A-7	Calculation of values of $-A_T\Delta\sigma$ and associated values of m_2^s/m_2 and $(m_2^s/m_2)m_o$	217-21
A-8	Residual lindane on adsorbent surface after differing time periods following application of a 50 mg/l benzene solution	222

GLOSSARY

In the following list, where the subscript i is employed, subscripts 1 or 2 are used in the text, 1 referring to the solvent and 2 to the solute.

a_i	activity of component i in the bulk phase
$a_i{}^s$	activity of component i in the adsorbed phase
A_i	molar cross-sectional area of component i as a monolayer
A	surface area of the adsorbent = A_T
c	equilibrium concentration of the solute in the bulk solution = c_2
c_o	saturated concentration of the solute in a specified solvent at a specified temperature
$c_2{}^s$	concentration of the adsorbed solute in the adsorbed phase
f_i	fugacity of component i in the bulk phase
$f_i{}^s$	fugacity of component i in the adsorbed phase
$\Delta \bar{G}^o$	$= \mu_2^{o,s} - \mu_2^o$
ΔG^a	integral change in free energy of the solid-solution interface due to adsorption
ΔG^B	integral change in free energy of the bulk solution due to the lowering of concentration accompanying adsorption
ΔG	integral change in free energy for the entire adsorption process
$\bar{H}_2^o$	standard partial molar enthalpy of the solute in the bulk phase
$\bar{H}_2^{o,s}$	standard partial molar enthalpy of the solute in the adsorbed phase
$\Delta \bar{H}^o$	$= \bar{H}_2^{o,s} - \bar{H}_2^o$
$\bar{H}_2^*$	partial molar enthalpy of the solute at zero pressure
$\bar{H}_2$	partial molar enthalpy of the solute in the bulk solution at equilibrium
$\bar{H}_2^s$	partial molar enthalpy of the solute in the adsorbed phase at equilibrium

GLOSSARY (cont.)

$\Delta \bar{H}_\sigma$	$= \bar{H}_2^s - \bar{H}_2$
$\bar{H}_s$	molar enthalpy of pure undissolved solute
$\Delta \bar{H}'$	$= \bar{H}_2^s - \bar{H}_s$
ΔH	integral change in enthalpy accompanying the adsorption process
k	constant in Freundlich isotherm equation; in specified places used also for Henry's law constant
k'	constant in Freundlich isotherm equation when c/c_o is plotted against x/m; in specified places used also for Henry's Law constant applied to the adsorbed phase
K_2	thermodynamic equilibrium constant for the solute alone
K_o	thermodynamic equilibrium constant for the total adsorption process
m_i	total mass of component i in the bulk solution
m_i^s	total mass of component i in the adsorbed phase
M_i	formula weight of component i
n	constant in Freundlich isotherm equation
n_i^o	total number of moles of component i in system
n_i^s	total number of moles of component i adsorbed in the monolayer
N	Avogadro's number
Q_Γ	isosteric heat of adsorption
R	universal gas constant
s	specific surface area of the adsorbent in cm^2/gm
$\bar{S}_2^o$	standard partial molar entropy of the solute in the bulk phase
$\bar{S}_2^{o,s}$	standard partial molar entropy of the solute in the adsorbed phase
$\Delta \bar{S}^o$	$= \bar{S}_2^{o,s} - \bar{S}_2^o$
$\bar{S}_2$	partial molar entropy of the solute in the bulk phase at equilibrium
$\bar{S}_2^s$	partial molar entropy of the solute in the adsorbed phase at equilibrium

GLOSSARY (cont.)

$\Delta \bar{S}_\sigma$	$= \bar{S}_2^s - \bar{S}_2$
$\bar{S}_s$	molar entropy of pure undissolved solute
$\Delta \bar{S}'$	$= \bar{S}_2^s - \bar{S}_s$
ΔS	integral change in entropy accompanying the adsorption process
T	temperature
x/m	mass of solute adsorbed at equilibrium per gram of adsorbent
$(x/m)_m$	maximum monolayer capacity of adsorbent for solute per gram of adsorbent
γ_i	activity coefficient of component i in the bulk phase
γ_i^s	activity coefficient of component i in the adsorbed phase
Γ_2	surface excess = excess of solute in the surface layer of unit area compared with the amount present in that quantity of the bulk solution which contains the same number of moles of component 1.
θ	surface coverage, defined as the fraction of the surface covered by the solute at equilibrium
μ_i	chemical potential of component i in the bulk solution
μ_i^s	chemical potential of component i in the adsorbed phase
μ_2^o	standard chemical potential of the solute in the bulk phase
$\mu_2^{o,s}$	standard chemical potential of the solute in the adsorbed phase
ρ_i	density of component i
σ	surface (or interfacial) tension
σ_i^o	interfacial tension at the solid-solution interface at the standard state for adsorbed component i
ϕ	spreading pressure, defined as $\phi = \sigma_s - \sigma$, where σ_s is the surface tension of the clean surface

INTRODUCTION

In recent years the importance to public health of the fate of pesticides in soil and water has become more evident. Numerous studies have been carried out in an attempt to find out the degree of persistence of applied herbicides, fungicides, and insecticides on crops and soils. These results suggest that intensive, relatively controlled laboratory experiments on the adsorption of an insecticide from solution onto soils would help to elucidate existing data on the field behavior of the insecticide.

The compound, γ-1,2,3,4,5,6-hexachlorocyclohexane and its beta isomer were chosen for study. Grades of the gamma-isomer which have a purity of 99% or higher have been given the name 'lindane' or 'Gammexane.' The gamma-isomer displays far greater insecticidal properties than the other isomers. Its lethal action on many insects is typically faster than that of DDT.[80] Lindane offers a definite health hazard for man. Dust applications of a mixture of the isomers, including the gamma-isomer, have been known to cause nausea, headache, and irritation of the skin, eyes, nose, and throat of workmen in the field. Lethal effects in rats have been reported when doses exceeding 0.1 - 0.2 grams γ-isomer per kilogram of body weight were given.[28]

Although a number of field experiments have been performed using lindane, practically no thorough laboratory experiments have been conducted with these isomers such as would reveal the nature and energetics of their adsorption on soils.

Lindane was chosen for a number of reasons. It has been shown to be relatively persistent in soils and it presents certain health hazards to man. Uptake of lindane by crop plants has been reported by several workers.[9,54,66,73,86,91] It is one of the chlorinated hydrocarbons more readily determined by electron capture gas chromatography, because of its short retention time. Further, the solubility of lindane in water, although low, is much higher than that of most other chlorinated hydrocarbons. Finally, the stereochemistry of lindane is important, and the prospect of comparing its adsorptive behavior with that of one of its stereoisomers presented an opportunity to examine in a broader sense the behavior of organic molecules in soil and water.

LITERATURE REVIEW

Lindane in soils

Considerable field work and some laboratory experiments have been performed in an effort to determine the behavior of lindane and other chlorinated hydrocarbons in soils. Bailey and White[3] have made a thorough research of the literature concerning soil-pesticide relationships including chlorinated hydrocarbons. Hadaway and Barlow[27] found that spray-applied lindane on blocks of red lateritic soil of Uganda diffused into the blocks rapidly at 90% relative humidity, but only very slowly at 10% relative humidity. Their results indicated that the transfer of lindane by volatilization from the dried spray to the soil in the remainder of the block took place only to a small extent. They believed the greatest movement occurred by diffusion directly from the crystals over the surface of the soil. They recovered lindane intact from the soil blocks.

Many workers have studied the persistence of lindane and related compounds in soil. Westlake and San Antonio[91] report a relatively low rate of loss of BHC from soil. They report that the concentration of BHC in air-dry soil reduced from 90 ppm to 30 ppm over a period of six years. (BHC refers to benzene hexachloride which is the term commonly, but incorrectly, applied to a mixture of isomers of 1,2,3,4,5,6-hexachlorocyclohexane, usually containing 10-12% gamma-isomer.) Lichtenstein and Schulz[50] reported that lindane breaks down in soil into a non-toxic product, possibly pentachlorocyclohexene. Two weeks after treatment of a muck, a silt loam, and a sandy soil, although 89% of the initially applied lindane was recovered colorimetrically, only

60% was determined present by bioassay. In their field experiments, 3 1/2 years after lindane was applied to soils, 10.7% was recovered by the Schechter-Hornstein (colorimetric) method, and of the amount so recovered, 46% was determined to be undecomposed lindane by bioassay. In other related experiments these authors[51] found that the persistence of lindane was most affected by soil types. Six months after application, 1.84 times more lindane was recovered from a muck soil than from a loam soil. This ratio increased to 8.45 three years following the original lindane treatment. The dissipation of lindane in several field soils in Ohio, Kansas, and Wisconsin was studied by Lichtenstein, DePew, Eshbaugh, and Sleesman.[49] They concluded that the insecticide was more persistent in dry soils than in moist soils. The percent organic matter of the soil and climatic conditions were seen to be the most important factors in insecticide persistence. Four and a half years after treatment, 15 to 29% of the originally applied lindane was recovered from muck soils by bioassay (depending upon the rate of application -- 10 or 100 lbs. per top acre six inches), whereas only 3 to 7% was recovered from sandy loam soils. Very low recoveries by bioassay (0-2.3%) were obtained with the two Kansas soils (both silt loam) after 4 1/2 years. A combination of high rainfall together with relatively low soil organic matter content probably contributed to the high loss of lindane from the Kansan soils.

Raghu and MacRae[72] in laboratory tests of γ-BHC-treated submerged soils found the rate of loss of the insecticide much less in sterilized soils than in nonsterilized soils over a period of 90 days following application. They concluded that biodegradation of γ-BHC on the two clay soils tested occurs under flooded conditions. Mulla[58] sprayed the surface of Coachella fine sand with lindane, thoroughly mixed the soil and stored it, covered, at 88 ± 2°F at a moisture level of 11-12%. After nine months he determined by bioassay that there had been no loss of activity of lindane. MacPhee, Chisholm, and MacEachern[54] measured the persistence of lindane in soil over a four-year period. They found that BHC had less persistence in soil than arsenic or DDT, but more persistence than chlordane. They found an average annual loss of 16% for BHC (containing 6% gamma-isomer).

Jameson and Peacock,[37] in field tests, applied 4% BHC (containing 13% gamma-isomer) as a dust at several rates to a medium loam soil. Six months after treatment at the rate of 8 lbs. of BHC per acre, 1.46 ppm were recovered in the top six inches of soil by colorimetric analysis, while after 36 months only 0.23 ppm were so recovered. Smith[82] conducted indoor and outdoor leaching tests with BHC-treated acid and alkaline sandy loam soils. Analyzing by means of bioassay and by means of alcoholic dehydrohalogenation followed by titration of excess HCl, he recovered about 80% of the BHC from the soils after an 18-month period. After 18 months the harmful effect of BHC on the root growth of wheat, cabbage, sugar beet and flax grown on BHC-treated soil was observed even at a BHC concentration as low as 0.02% (relative to soil weight). Randolph, Chisholm, Koblitsky, and Gaines[73] conducted field tests with BHC applied to Miller clay in Texas for four years. The equivalent of dosages of BHC normally applied to cotton fields over a five-year period was applied as an initial dosage (61 lbs. per acre) followed by an application of 6-9 lbs. per acre each succeeding year. Analysis by means of an organic chlorine method revealed that 76-87% of the applied BHC was lost annually.

A few workers have studied the effect of various leaching regimes on the movement and adsorption of lindane in soils. Lichtenstein[48] placed two layers of soil containing 10 ppm lindane over three cheesecloth-separated untreated soil layers in cartons with perforated bottoms. Each layer consisted of 150 grams of soil. Water treatments varied from none for ten days, 100 ml daily for five days, to 100 ml daily for ten days. After 5 (or 10) days the columns were cut open and the different layers separated and analyzed by the colorimetric method. Under leaching conditions lindane moved most in the Plainfield sand (1.31 ppm found in the third layer) and least in the muck (0.15 ppm in the third layer), while the movement was intermediate in the Miami silt loam. Where no water was applied no lindane was recovered in the lower three layers in Plainfield sand. But diffusion apparently occurred under non-leaching conditions in Miami silt loam (0.27 ppm found in the third layer) and in the muck (0.80, 0.16, and 0.14 ppm in the third, fourth, and fifth layers, respectively). No lindane was determined in the filtrate. Gargantini, Gianotti, and DeTella[23] applied five grams of 1% and 12% BHC to the surface of a slightly acid sandy loam soil in 40 cm. deep lysimeters. After six months of gently applying a total of 1,079 mm. of water, about 90% of the BHC was found to be retained in the top 10 centimeters and about 0.4% in the bottom layer.

Press[70] studied the adsorption and movement of lindane in columns using 27 different East African soils. Forty milligrams of lindane in 8.4 ml of isohexane were applied to the top of each column containing five grams of soil. After removing the filtrate for analysis, the columns were washed with further portions of isohexane until essentially all the lindane was removed. Analysis was carried out by determination of the weight of the eluted lindane. Amounts adsorbed varied (with the kind of soils) from 2.21×10^{-5} to 9.60×10^{-5} moles of lindane per gram of soil. On aluminum oxide (Brockmann activity of 2-3) 23.09×10^{-5} moles per gram were adsorbed. Volumes of solvent required to elute essentially all the adsorbed lindane varied from 3.36 to 6.72 ml per gram of soil. The only correlation of adsorptive capacity to soil properties concluded by the author was that finely particulate soils were relatively more adsorptive.

Swanson, Thorp, and Friend[83] studied adsorption of lindane in a similar manner. Twenty-five ml of a 1% solution of lindane in petroleum ether were pipetted into columns each containing 50 (or 100) grams of soil. The eluate was collected and after the solution had leached through to the top level of the soils, the columns were leached with five aliquots of petroleum ether weighing the equivalent of the weight of the soil used. Analysis consisted of evaporating the eluate to dryness and weighing. Exchange resins were found to hold no lindane; thus, the influence of the soil exchange complex in lindane adsorption was concluded to be small. The presence of organic matter in soil seemed to have little effect in increasing lindane adsorption. The amount of lindane adsorbed, however, was closely correlated to percent clay content of the soil. (A loamy sand held 0.014 grams per 100 grams of oven-dry soil, while a silty clay loam held 0.214 grams per 100 grams of soil.) An unexplained correlation between exchangeable magnesium and lindane adsorption was obtained. Volatilization loss from soil containing 1% lindane was measured after oven-drying and after moist autoclaving. The greatest amount of lindane was lost from soils during the autoclaving. Apparently water replaced lindane on the soil surface during autoclaving. Soils high in capillary porosity lost the least amount of lindane during the heat treatments.

Adsorption of organic compounds on soils and clays

Adsorption may be defined as the concentrating of a particular component at any interface.[42] If we consider the interface at the soil or clay surface, considerable work has been done in the study of the adsorption of organic compounds. As examples of studies on the adsorption of gaseous organic compounds on evacuated clays and soils, Jurinak and Volman studied the adsorption of ethylene dibromide vapor,[38,39] n-butane vapor,[40] and the vapors of 1-chloroethylene, trans-1,2-dichloroethylene, and trans-butene-2 on natural soils, montmorillonites, and kaolinites.[41] Adsorption of ethylene dibromide was shown to be essentially restricted to the external surface of the clay minerals. Eberly investigated the adsorption of benzene, cyclohexane, and n-hexane in the gas phase on mordenite.[16] He found Na-mordenite to have an exceptionally high adsorptive capacity for the hydrocarbons in the temperature range studied (90°-200°C).

Many studies have also been carried out on the adsorption from solution of organic compounds on soils and clays. The adsorption of ionizable organic compounds, such as organic acids and amines, from solution onto clays and soils have been investigated by many workers. Hendricks[32] studied the adsorption of organic cations on montmorillonite. He found that many of the organic compounds gave the same value for exchange capacity of the clay as that obtained by the use of inorganic cations. But large organic molecules such as brucine exhibited a 'cover-up' effect and so yielded lower values for exchange acpacity. Hendricks concluded that while the normal coulombic forces involved in cation exchange were operative in the adsorption, Van der Waals forces were also believed important because of the number of organic cations showing co-planar adsorption by X-ray analysis. Greenland, Laby, and Quirk[25] have recently studied the adsorption of amino-acids and peptides on montmorillonite and illite. Frissel[21] has studied the adsorption of ionizable herbicides from aqueous solutions on clay minerals. He found that at very low pH all the compounds were adsorbed strongly. His data indicate the importance of non-coulombic forces as well as coulombic forces in the adsorption of ionizable compounds. Harris[31] studied the adsorption and desorption of herbicides from aqueous solutions in soils. Most of the compounds he studied were ionizable in water. He found that while adsorption of the herbicides on bentonite was greater at 0°C than at 50°C, the extent of adsorption by muck was the same at both temperatures. Some irreversible adsorption was indicated in the case of the muck.

Talbert and Fletchall[84] studied the adsorption on soils of s-triazines, which are in general very weak bases with relatively low water solubility. They found that the ratio of the amount of herbicide adsorbed to the amount in the equilibrium solution remained relatively constant over a range of concentrations. Increasing the temperature reduced the adsorption of simazine and atrazine. No adsorption was detected for simazine and atrazine on kaolinite. Organic matter was generally more adsorptive than clays. Upchurch and Mason[87] found that for 12 herbicides tested there was a positive linear relationship between the percentage of soil organic matter and the amount of herbicide required to add to the soil to produce a 50% growth reduction of cotton.

Phillips[69] determined isotherms for the adsorption of ethylene dibromide and phenol from aqueous solutions onto three soils. The isotherms in all cases were roughly linear. For a given soil, the slopes of the isotherms for the two compounds corresponded closely. The slopes of the isotherms for a given compound correlated most closely with the percent organic matter in the soil.

Nose, Suzuki, and Fukunaga[61,62,63] did research on the behavior of pentachlorophenol in 14 soils and 4 clays. Within a certain range of concentration, Freundlich's equation ($A = kc^n$) applied for adsorption from aqueous solutions. Maximum 'k' values were found for an acid clay. Increasing acidity led to greater adsorption on mineral soils. The authors concluded that pentachlorophenol is adsorbed on the mineral part of the soil in its non-ionized form. At high pH they believed humus to be generally responsible for its adsorption (in this case, as an ion). The presence of organic matter is important for pentachlorophenol (PCP) adsorption in soil. The adsorption of PCP on H_2O_2-treated soil and on subsurface soil low in humus was found to be very slight. The same authors[64] studied the adsorption of phenols on Fuller's earth. From the relationship discovered between pH and adsorption, they concluded that phenols are generally adsorbed as the molecular form (not ionized) on the clay.

Because of the fact that the compounds chosen for the present study are non-ionizable, particular attention should be given to studies of adsorption from solution in which the contribution of coulombic forces to adsorption is nil. (Adsorption would be assumed to be the result of Van der Waals-type forces alone.) Phillips' study of the adsorption of ethylene dibromide from solutions and the study by Nose, et al., of undissociated PCP adsorption, just referred to, are examples of this. Bradley,[8] on the basis of X-ray diffraction data, concluded that polar organic molecules are held to a clay surface through a C-H ····O bond. Mac Ewan[53] concluded from his X-ray studies that the organic adsorbate must contain some polar groups in order for inter-layer adsorption to take place on montmorillonite. Hoffmann and Brindley,[34] in studying the adsorption of aliphatic compounds from water on montmorillonite, found that molar adsorption increased with chain length from 5 to 10 carbons. Beyond 10 carbons, increase in chain length didn't seem to affect adsorption appreciably. Brindley, Bender and Ray[10] investigated the adsorption of acetoaceticethylester and β,β'-oxydipropionitrile from aqueous solutions on montmorillonite, kaolinite, and gibbsite. They found that adsorption in relation to adsorbent surface area was largest for gibbsite, and lowest for montmorillonite, with adsorption on kaolinite being intermediate. Two possible explanations are put forth: (1) the adsorption energy for organic molecules is greater on hydroxyl surfaces than on oxygen surfaces; and (2) the competing water molecules are adsorbed more strongly on oxygen surfaces (as on montmorillonite) than on hydroxyl surfaces. Zhdanov, Kiselev, Novikova, and El'tekov[94] conducted research on the adsorption of thiophene from solutions in n-heptane and benzene on synthetic faujasite. They found that adsorption of thiophene from dilute n-heptane solution increased when 25 to 50% of sodium ions on Na-faujasite were replaced by calcium ions. They found the isosteric heat of adsorption of thiophene from n-heptane at low concentrations to be of the order of 5 kcal per mole. Positive adsorption of thiophene from benzene solutions occurred only up to $X_2 = 0.05$, where X_2 is the mole fraction of thiophene. At high thiophene concentrations, there was positive benzene adsorption.

Weidhaas[89] investigated the adsorption of DDT and structurally related chlorinated hydrocarbons on insecticide dust diluents. He found appreciable adsorption from hexane solutions, less from benzene solutions, and none measurable from ethanol solutions. Other things being equal the extent of adsorption was greater on adsorbents which had been oven-dried. In the equilibrium concentration range of 0.5 to 2.5 mg. per ml, the isotherms ($T \cong$ constant = room temperature) of the adsorption of DDT from hexane were roughly linear. For the adsorbents used, the slope of the isotherm increased in the following order: Celite 209 (a diatomaceous earth) < Barden clay (a kaolinite) < Panther Creek bentonite < Diluex A (an attapulgite). This order held for all the organic species tested and for both benzene and hexane solutions. Methoxy-DDE and methoxychlor were adsorbed to approximately the same extent. Both were adsorbed significantly more on all diluents than DDT. DDE was the least adsorbed of the components tested. DDA (ionizable in water) was adsorbed to the greatest extent. Reaction with the surface to produce catalytic change (possibly dehydrohalogenation) was observed in the case of methoxychlor and methoxy-DDE on the attapulgite, the bentonite, and the kaolinite.

Riggs[74] studied the adsorption of p,p-DDT on bentonites (2% suspensions) from solutions more dilute than those of Weidhaas. He found that for all solvents Na-bentonite adsorbed somewhat more DDT than Ca-bentonite (both bentonites of particle size 0.2 to 1.0 micron). Adsorption of DDT was least on raw bentonite with unsegregated particle size. Equal amounts of the compound were adsorbed from benzene and from n-hexane.

Adsorption levels were less when DDT was adsorbed from 95% ethanol and even less from a mixed benzene-water (50-50) system. Slight decreases in adsorption of DDT from benzene were observed when the temperature was increased from 25°C to 35°C.

The chemistry of the BHC isomers

Crude BHC is produced by combining chlorine and benzene (in a molar ratio of 3 to 1) in the presence of actinic light.[28] Out of a total of eight isomers, five have been found to be present in crude BHC in relatively consistent proportions. Table 1 gives the melting points of these five (most common) isomers together with the percentage composition in crude BHC.

Table 1

Melting points and percent composition in crude BHC of the five most common isomers[80]

Isomer	Content in crude BHC (%)	Melting point (°C)
α	55 - 70	157 - 158
β	5 - 14	309
γ	10 - 13	112
δ	6 - 8	138 - 139
ϵ	3 - 4	218 - 219

The formula weight of the BHC isomers is 290.86. The density of γ-BHC has been determined by X-ray measurement to be 1.88.[1] The crystals of BHC isomers are colorless. A slight tendency for sublimation of the gamma isomer crystals at its melting point has been reported.[1]

A planar configuration of the carbon atoms is not possible for cyclohexane and its derivatives because a bond angle of 120 degrees between carbon-carbon bonds would be required, rather than the normal tetrahedral angle of 109° 28'. Thus, a 'puckered' form -- either the 'boat' configuration or the 'chair' form -- is assumed, which keeps the inherent bond strain of the ring to a minimum. It has been determined that the chair form of cyclohexane is more stable than the boat form because in the former configuration the non-bonded interactions are at a minimum.[13] The boat form of cyclohexane has been shown to have an energy content 5.33 kcal per mole greater than the chair form.[13] There are two categories of substituents placed on the cyclohexane ring. Axial substituents are those which project directly up or down from the ring. The equatorial substituents project outward, representing roughly an extension of what might be considered the plane of the ring. The isomers of BHC have been designated by Greek letters in the order of their discovery, without any intention to indicate their structure. For any isomer in the chair form there are two possible conformations. If one ignored the effect of non-bonded interaction in a molecule of a BHC isomer, the energy barrier to convert from one chair conformation to the other would be small. In such an interconversion the molecule 'flips over' and the axial and equatorial substituents in the original chair become equatorial and axial, respectively, in the new conformation.[13] It is known that the more chlorine atoms found in the axial position the less stable the conformation is.[29] Consequently, since the conformational equilibria lie almost entirely on the side of the more stable conformer, the isomer in each case is represented by the conformer with the most equatorial chlorine substituents. The positions of the chlorine atoms in each isomer (stable conformer) of BHC are indicated in Table 2.

Table 2

Conformations of Isomers of BHC[29]

Positions of Chlorine atoms*	Isomer
a a e e e e	α
e e e e e e	β
a a a e e e	γ
a e e e e e	δ
a e e a e e	ε
a a e a e e	ζ
a e a e e e	η
a e a e a e	ι

* 'a' indicates axial position
  'e' indicates equatorial position

Hanack[29] notes that if three chlorine atoms are axial, as in γ-BHC, then due to the proximity of the substituents a distortion of the tetrahedral angles of the molecule occurs. Van Vloten, Kruissink, Strijk, and Bijvoet,[88] however, concluded from their study of the crystal structure of the gamma-isomer that the steric hindrance causes only a slight bending apart of the 1,3-C-Cl bonds (chlorine in both bonds being in the axial positions).

Figures 1 and 2 are photographs of models representing the molecules of the gamma- and beta- isomers of BHC. In figure 2, depicting the beta-isomer, it is obvious that all six of the hydrogen atoms (represented by the white balls) are axial, and all six of the chlorine atoms are

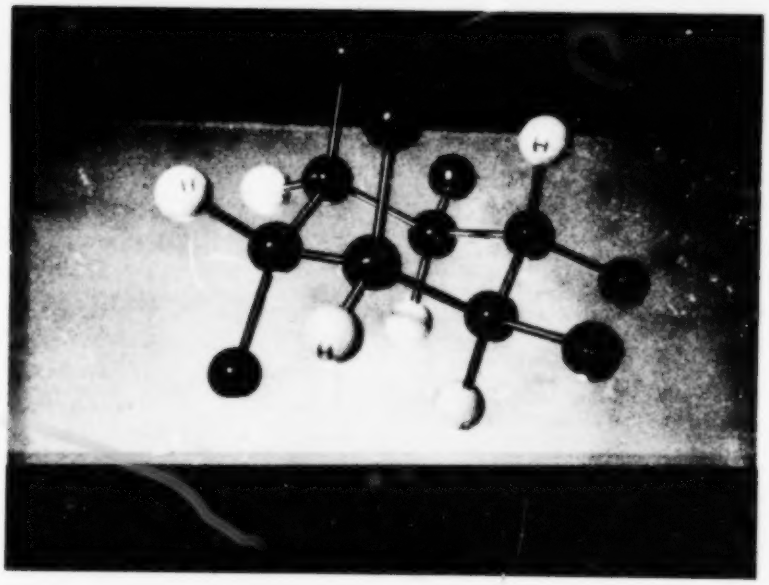


Figure 1. Molecular Model of γ-BHC.

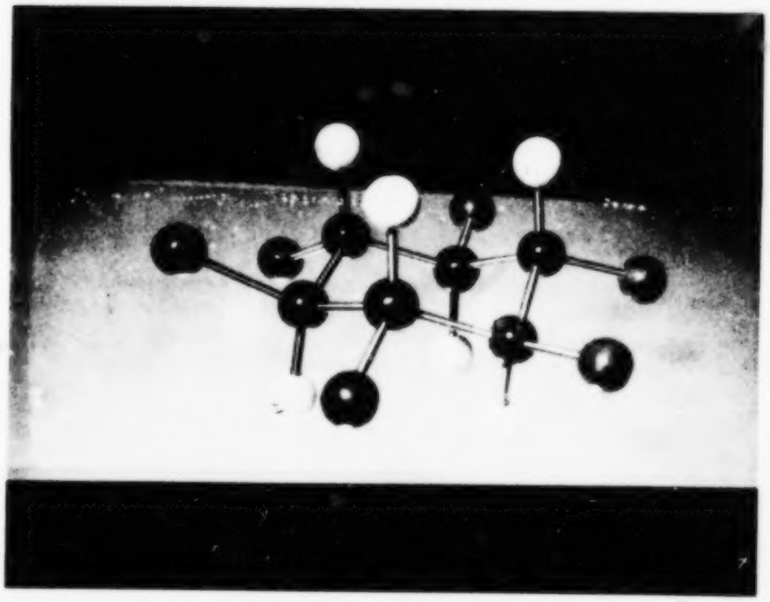


Figure 2. Molecular Model of β-BHC.

equatorial -- more or less in the plane of the carbon atoms (black balls). In figure 1 it is clear that in the gamma-isomer molecule three adjacent chlorine atoms are axial (two projecting up and one down) and three are in the equatorial position.

There is evidence that under some conditions interconversion between BHC isomers occurs. Klosa[44] irradiated samples of the α-, β-, and γ-isomers with ultraviolet light at elevated temperatures in the presence of heavy metal catalysts. But none of the isomers were determined to have transformed into other isomers. Elias, Lieser, and Kohlschütter[18] heated individual C^{14} tagged-BHC isomers with $AlCl_3$ in 1,1,2,2-tetrachloroethane. Their results showed that isomerization proceeded by equilibrium reactions according to the scheme: γ- $\rightleftharpoons$ δ- $\rightleftharpoons$ α-isomer. In the temperature range of 100-130°C, this equilibrium was shifted in favor of the α-isomer. After 18 hours of heating γ-BHC (C^{14}) at 99.4°C with $AlCl_3$ in $(CHCl_2)_2$, the percent composition of the α-, β-, γ-, and δ-isomers was found to be 9.4, 5.4, 29.9 and 55.3, respectively. Whetstone, Davis, and Ballard[93] reported isomerization to occur when heating single isomers with anhydrous $FeCl_3$ in sealed tubes under nitrogen at temperatures of 140°C or higher. Under these conditions, the α-isomer was the most stable. Pure γ-isomer was converted largely to the α- and δ-isomers. After a reaction time of 24 hours at 170°C, pure β-isomer yielded 77.3% α-, 13.0% β-, 1.3% γ-, and 2.7% δ-isomer.

Benzene hexachloride undergoes dehydrohalogenation in alcoholic alkali to yield a mixture of three tri-chlorobenzenes.

$$C_6H_6Cl_6 + 3OH^- \longrightarrow C_6H_3Cl_3 + 3Cl^- + 3H_2O .$$

BHC exhibits high stability, however, in the presence of strong mineral acids. Haller and Bowen[28] reported that unlike DDT it is not known to decompose when heated (below 115°C) with traces of metal, such as iron and aluminum, or their chlorides. However, Nakajima, Inagaki, and Tati[59] reported that the BHC isomers reacted with zinc dust (not granular zinc) at 30°C in the presence of water to produce the calculated amount of benzene in accordance with the equation

$$C_6H_6Cl_6 + 3\ Zn \longrightarrow C_6H_6 + 3\ ZnCl_2.$$

Less rapid reactions were observed using Fe and Sn. They reported that γ-BHC had the highest velocity reaction followed by the α-isomer and then the δ-isomer. The β-isomer did not react under these conditions.

Orlowski, Mazankowa, and Eckstein[68] obtained a 64-70% yield of trichlorobenzenes when heating BHC isomers at 280-300°C with no catalyst, 70-75% yield at 190-230°C with $AlCl_3$ as catalyst, and 80% yield at 215-230°C with an active carbon as catalyst. Eckstein, Mazankowa, and Orlowski[17] reported that at a temperature of 300°C and at a flow rate over active carbon of 0.5 to 1.0 kg per hour, dehydrohalogenation of BHC isomers was almost complete, but at 1.5 kg per hour unchanged BHC appeared in the products. After 110 hours the products consisted of 80% trichlorobenzenes and 7% tetrachlorobenzenes.

West and Campbell reported that dehydrochlorination of BHC occurs in the presence of alkalis even such as lime water at ordinary temperatures.[90] Alkaline dehydrochlorination of the α- and γ-isomers in water has been reported by Daviaud and Viel.[14] Werner and Waldichuk[92] studied the decay of the γ-isomer in 50% sea water and 50% distilled water. They found the decomposition rate higher in pure sea water than in the 50-50 mixture. By utilizing Millipore filters they were able to determine that the reaction was a chemical one, not dependent upon marine organisms. They employed by way of analysis the method of Hancock and Laws [Analyst 80,665-74 (1955)] . In week-old mixtures of BHC and sea water they were unable to detect the presence of di-, tri-, or tetra-chlorobenzenes. Thirty days after combining BHC isomers with sea water and storing in polyethylene bottles, the isomers were found present in the following percentages of the original concentration of the respective isomer: alpha 57%, beta 40%, and gamma 15%.

Hughes, Ingold, and Pasternak[35] studied the kinetics of elimination (dehydrochlorination) from the α-, β-, γ-, and δ-isomers of BHC in the temperature range - 27° to 90°C. They report the activation energies for the reaction for each isomer as determined by Cristol, Hause, and Meek [Jour. Amer. Chem. Soc. 73,674 (1951)] . The fact that the Arrhenius activation energy for the β-isomer is 32 kcal per mole, about 12 kcal/mole greater than that for the other three isomers, is explained by the fact that all the chlorine atoms are in equatorial positions in the β-isomer. Thus, the assumed preferred 1:2- elimination (trans) is not possible, and the energetically less preferred one (cis) must occur. In their experiments the initial concentrations of BHC was about 0.002 M and that of OH^- about 0.01 M. They found that in all cases the reaction is second order in hydroxyl ion and BHC isomer concentration. Their results indicate that the dehydrochlorination reaction occurs in three separate elimination steps resulting in the production of, consecutively, a pentachlorocyclohexene, a tetrachlorocyclohexadiene, and trichlorobenzenes. The intermediate δ-pentachlorocyclohexene (from the original δ-isomer of BHC) and γ-pentachlorocyclohexene (from the γ-isomer) were recovered and isolated. The final products, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,3-trichlorobenzene, were recovered in the following percentage compositions: from the β-isomer, 82.0%, 13.8%, and 4.2%; and from the γ-isomer, 78.2%, 17.6%, and 4.2%, respectively. These same authors reported that the rate constants for the reaction for all but the β-isomer decreased only slightly as the percent water in the ethanol reaction solution increased from 0 to 20%. They observe that this is in accord with the theory of kinetic solvent effects wherein no large effects are expected to arise from even a considerable change in solvent polarity.

The metabolism of BHC upon administration to mammals or insects has been shown to yield products which are often considerably different from those derived from purely chemical treatments. Menzie has reviewed research on the metabolism of BHC.[56] Production of all six isomers of dichlorothiophenol was indicated in two studies on the metabolism of γ-BHC in flies. Menzie refers to other studies in which both γ-BHC and γ-2,3,4,5,6-pentachlorocyclohexene were converted by rats into 2,3,5- and 2,4,5-trichlorophenol.

Schwabe[78] has studied the thermodynamics of solution for the isomers of BHC in benzene and acetone. He reports that the integral heats of solution of one gram of a BHC isomer in 100 grams of benzene for the α-, β-, γ-, and δ-isomers are, respectively, 4.2, 6.0, 4.8, and 3.0 kcal/mole. The differential thermodynamic properties which he determined for the solution of the α-, β-, γ-, and δ-isomers in benzene are shown in Table 3. Somewhat lower values for $\Delta \bar{H}$ and $T \Delta \bar{S}$ were observed for the isomers when acetone was the solvent. Schwabe and Legler[79] reported the heats of sublimation of the α-, β-, γ-, and δ-isomers as 23.4, 26.4, 21.4, and 23.1 kcal/mole, respectively.

Table 3

Thermodynamic properties of solution of BHC isomers at a concentration of one gram per 100 grams of benzene[78]

Isomer	$\Delta \bar{\bar{H}}$ (cal/mole)	$\Delta \bar{\bar{G}}$ (cal/mole)	$T \Delta \bar{\bar{S}}$ (cal/mole)
α	13.0	- 4.8	17.8
β	16.3	- 1.95	18.2
γ	14.6	- 6.30	20.9
δ	9.3	- 6.5	15.8

Several workers have measured the dipole moments of the BHC isomers. The results are summarized in Table 4.

Table 4

Dipole Moments of BHC Isomers (debye units)

Isomer	in benzene at 30°C[52]	in 1,4-dioxane at 30°C[52]	in benzene[67]	in benzene at 30°C[57]	in benzene at 20°C[71]
α	2.16	2.34	2.56	2.22	2.18
β	0.34	0.46	0	0	~0
γ	2.84	3.00	3.22	2.80	2.84
δ	2.24	2.32	2.66	2.22	2.22
ε	0.43	0.45		0	~0

The small moment for the β-isomer observed by Lind, Hobbs, and Gross[52] is believed by them to be indistinguishable from zero within experimental error. They note that since the β-isomer has been shown to be centrosymmetric, one would expect the electric moment to be zero. One of the conclusions of Quivoron and Néel[71] is that in a molecule of this type the effective moment of the C-Cl bond may vary within rather large limits (once to twice) on account of induction effects. Because of mutual polarization between adjacent C-Cl bonds it is not possible to estimate the total moment of the molecule by simply adding the vectors of the moments for the single C-Cl bonds and C-H bonds.[71]

The vapor pressures of the BHC isomers have been measured. Generally the values reported by Slade[81] are considered too high, but they are included in Table 5 for purposes of comparison.

Table 5

Vapor Pressures of the BHC Isomers
(measured at 20°C in mm. Hg)

Isomer	Investigator	
	Slade[81]	Balson[4]
α	2×10^{-2}	2.5×10^{-5}
β	5×10^{-3}	2.8×10^{-7}
γ	3×10^{-2}	9.4×10^{-6}
δ	2×10^{-2}	1.7×10^{-5}

These values may be compared to the vapor pressure of p,p'-DDT of $\sim 1.7 \times 10^{-7}$ mm Hg at 20°C.

The solubilities of the four common BHC isomers in various solvents were measured by Slade.[81] A few representative values for the β- and γ-isomers are given in Table 6.

Table 6

Solubilities of the β- and γ-isomers at 20°C in grams per 100 grams of solution[81]

Solvent	β-isomer	γ-isomer
Acetone	10.3	43.5
Benzene	1.9	28.9
Cyclohexane	0.8	4.6
Pentane	0.1	2.2
Petrol Ether (60-80°)	0.2	2.7
Acetic acid	1.0	12.8
Ethyl alcohol	1.1	6.4
Distilled water	(5 ppm)	(10 ppm)

Most workers have reported the solubility of γ-BHC in water to be in the range of 7.0 to 8.5 ppm. Sazonov, Bogdarina, and Gudkova[76] were able to obtain a maximum solubility in water of 31.8 ppm by stirring over a long period of time. Riggs,[74] analyzing by means of electron-capture gas chromatography, has found the solubility of the γ-isomer in distilled water to depend not only upon the temperature but also upon the maximum effective particle size of the compound in water. The maximum effective particle size is the upper limit of solute particle sizes which are considered to be dissolved. The maximum effective particle size was varied by employing differing centrifugation speeds prior to sampling and analysis. Table 7 summarizes his results.

Table 7

Influence of maximum effective particle size of solute and of temperature upon the solubility of γ-BHC in distilled water[74]

Max. particle diameter of γ-BHC in water (microns)	Solubility in micrograms per liter Temperature (^{o}C)			
	15	25	35	45
0.01	75	150	315	575
0.05	330	600	950	1,450
5.0	2,150	6,800	11,400	15,200

The drastic reduction in the solubility of γ-BHC with reduction in solute particle size raises a doubt as to whether the compound is genuinely dissolved at all in water.

Before the advent of gas chromatographic analysis, the most reliable and specific method for determining γ-BHC quantitatively was the colorimetric method described by Schechter and Hornstein [Anal. Chem. 24,544 (1952)]. At the present, by employing electron-capture gas chromatography the presence of the BHC isomers in a solution concentration as low as a few parts per billion may be detected, and reliable quantitative analysis is achieved with concentrations of 30 to 50 ppb or greater. Oda, Norishima, and Uchijima[65] used Thermol-2 as the stationary fluid in a stainless steel gas chromatographic column at a flow rate of 45 ml per minute and found that the relative retention times of the α-, β-, γ-, and δ-isomers were 0.796, 1.107, 1.00 and 1.331, respectively. Guillemin[26] employed a stainless steel column packed with 40-60 glass beads coated with 25%, by weight, polypropylene glycol Niax 1025 and used a helium flow rate of 5 liters per hour. He found the relative retention times for the α-, β-, γ-, δ-, and ϵ-isomers were 0.674, 1.76, 1.00, 2.27, and 2.05, respectively.

THEORETICAL CONSIDERATIONS

Nature of adsorption from solution

Adsorption on a solid adsorbent from a binary solution is obviously more complex than adsorption of a gas on such an adsorbent. In addition to the interaction of solute and adsorbent, one must take into consideration solvent-adsorbent and solvent-solute interactions. The adsorbate may be considered either the solute or the solvent, or both. Adsorption from such a solution can be viewed as a competitive process in which solvent and solute molecules compete for sites on the adsorbent. If the adsorbent is heterogeneous, however, due to structural and electrical differences between solute and solvent molecules, certain sites may be specific for one or the other species. Thus, for those sites little competition would be involved. Most adsorbents are of a heterogeneous nature in which site types and energies vary to some extent. For example, considering soils as adsorbents, site energies are known to vary in the clay fraction, and drastic differences in site type occur considering the functional groups of the organic fraction compared to the oxygen and hydroxyl surfaces of the clay fraction. Adsorption of a solute molecule necessitates desorption of one or more solvent molecules, depending on their relative size. In the case of the adsorption of BHC from water, since the BHC molecule is estimated to have a cross-sectional area approximately four times that of a water molecule, in general four water molecules must be desorbed in order for one BHC molecule to be adsorbed at the solid surface.

We shall restrict our discussion to a consideration of the adsorption of non-charged species from solution on solid surfaces. We shall assume, then, that coulombic forces play essentially no part in the adsorptive process. And, if no chemical reaction occurs concurrent with adsorption, the forces involved in adsorption can be considered to be Van der Waals forces alone. Van der Waals forces comprise those forces involved in dipole-dipole interactions and dipole-induced dipole interactions, as well as the so-called London dispersion forces. Frissel[21] has pointed out that adsorption of organic molecules from aqueous solutions due to dipole-dipole interaction should be rather small because water, which would be displaced, has a large dipole moment itself. He believes that the adsorption energy due to induction forces (dipole-induced dipole) is also small.

Cassidy's review of the literature on adsorption[11] leads one to believe there is no clear correlation between an adsorbate's permanent dipole moment and its adsorbability. It does appear from his review, however, that with increasing polarizability of the adsorbate, adsorption on polar adsorbents from nonpolar solvents does tend to increase. Nose, Suzuki, and Fukunaga,[60] in studying the adsorption of p-substituted nitrobenzenes on soils, observed that the ratio of the amount adsorbed to the equilibrium concentration increased with an increase of dipole moment when the substituent was an electron repulsive group. But when the p-substituent was an electron attracting group the ratio decreased with an increase of the dipole moment.

The energy due to dispersion forces according to the London model is inversely proportional to the third power of the distance between the adsorbable molecule and the surface.[30] Frissel[21] believes these forces may be of great importance. Because the dispersion forces affect all the atoms of the adsorbent and adsorbate, all polyatomic molecules will tend to assume a coplanar orientation with respect to the adsorbing surface. Frissel presents the equation given by Verwey and Overbeek (Theory of the Stability of Lyophobic Colloids, Amsterdam, 1948) for the dispersion interaction between an adsorbed particle and a planar surface as

$$E_d = \pi q \lambda / 6 \left[1/R^3 - 1/(R + \delta)^3 \right] , \qquad (1)$$

where E_d is the energy of adsorption due to dispersion forces, q equals the total number of ions per cm^3 of the clay crystal, R equals the distance from the center of the adsorbed particle to the clay surface, δ is the thickness of the clay crystal, and λ is a function of the polarizabilities and ionization potentials of the adsorbed particle and of the clay lattice ions.

Adsorption may be treated in accordance with a potential theory. Polanyi described potentials arising from dispersion forces [Z. Physik 2,111 (1920)]. In such theories the adsorptive forces are seen as operating over a diffuse layer in accord with an equation similar to (1). The concentration ofthe adsorbable species then decreases with the distance from the solid-solution interface according to a Boltzmann-type distribution. At a certain (small) distance from the surface, the interaction of the attractive forces and the repulsion forces create a minimum potential energy. Adsorbed molecules in the region of the minimum potential energy may be considered as having been on the average more energetic than the molecules remaining in the bulk solution. Such adsorbed molecules must have sufficient energy to overcome the force accompanying the tendency toward diffusion away from the interface. With such a model the definition of adsorption cannot be limited to the solid-solution interface, but must include as well a description of the changes of solution concentration with distance from the surface.

Hansen and Mai[30] developed equations for isotherms by combining the Polanyi-London potential theory in a general theory of adsorption from regular solutions.

For the purposes of this thesis we will treat adsorption as occurring in a monolayer immediately at the solid-solution interface. The bulk solution concentration will be considered to remain constant with distance from the adsorbed monolayer. Assuming that the London dispersion forces predominate and that the corresponding energy is inversely proportional to the third power of the distance from the surface, we may estimate the relative effect of such forces beyond a monolayer. We shall ignore the effect of repulsion forces. Further, the distance from the surface will be considered to be measured from the outer surface of the surface atoms of the adsorbent, not from their centers. Then, assuming a 'clean' surface, having no adsorbed film, the energy of attraction at a distance of 4 Å (one-half the approximate thickness of adsorbed BHC molecules) would be proportional to $1/(4)^3$. At the centers of the hypothetical 2nd and 3rd layers, the energies of attraction would correspondingly be proportional to $1/(12)^3$ and $1/(20)^3$, respectively. Thus, the second layer would experience a maximum attractive energy only 3.7% of that of the monolayer, and the third layer would experience a maximum energy only 0.8% of that of the monolayer. Considering that the relative energy of the 2nd and 3rd layers would be even lower than this upon the actual adsorption of an adsorbate, it is not unreasonable to neglect the attractive energies beyond the monolayer and to assume, as a working model, that adsorptive forces are experienced only in the single monolayer at the interface.

Adsorption isotherms

The adsorption isotherm delineates the equilibrium positions for a given system at a constant temperature over a certain range of concentrations. Each point on the isotherm represents an amount adsorbed in equilibrium with the corresponding concentration of the bulk solution.

Several workers have pointed out that unless one takes account of the dilution effect in the bulk solution due to the desorption of the second component (during the adsorption of the first), the resulting isotherm is what is termed a composite isotherm.[42] That is, a simple subtraction of the equilibrium concentration from the initial concentration of the bulk solution will not yield, strictly speaking, the isotherm for a single component. Rather, the result will be a composite isotherm, in which the effects of the adsorption of one component and the desorption of the other are combined. The values obtained for the amounts of solute adsorbed will be higher than the actual amounts adsorbed. Discussion of this point is perhaps worthwhile at this time.

Let us consider the number of moles of the solute ($n_2{}^*$) transferred from the bulk solution to the monolayer during the adsorption process. Thus, $n_2{}^*$ is equal to the number of moles of adsorbate adsorbed over and above what would be present in the monolayer on the basis of the initial concentration. It is evident, then, that

$$n_2{}^* = n_2{}^s - (n_2{}^o/n^o)\, n^s \qquad (2)$$

where $n_2{}^s$ is the total number of moles of solute adsorbed in the monolayer at equilibrium, $n_2{}^o$ is the total number of moles of solute in the system, n^o is the total number of moles of solute and solvent, and n^s is the total number of moles of both species in the monolayer at equilibrium. The bulk solution will be considered to extend only up to the adsorbed monolayer. For dilute solutions it can be shown that the amounts of solute adsorbed as calculated simply from the difference between the initial and equilibrium concentrations approximate the true values for n_2^*. Accordingly, the composite isotherm would correspond closely with the isotherm for the component exhibiting preferential adsorption. At time zero, when the solution is combined with the adsorbent and before any adsorption has occurred, we have

$$n_1/n_2 = n_1^o/n_2^o, \tag{3}$$

where n_1 and n_2 are the number of moles of solvent and solute in the bulk phase, and n_1^o and n_2^o are the total number of moles of solvent and solute added. One must note that because the monolayer at the solid-solution interface is not considered part of the bulk solution, $n_1 < n_1^o$ and $n_2 < n_2^o$.

Let us assume that A_2/A_1 is an integer, where A_2 and A_1 are the molar cross-sectional areas of monolayers of the solute and solvent, respectively. Then, from time zero until equilibrium is attained a total of n_2^* moles of solute are transferred from the bulk solution to the monolayer, while correspondingly $(A_2/A_1)\ n_2^*$ moles of solvent are transferred from the monolayer to the bulk solution. At equilibrium the number of moles, n_1' and n_2', of the solvent and solute in the bulk phase would therefore be

$$n_2' = n_2 - n_2^* \tag{4}$$

$$n_1' = n_1 + (A_2/A_1)\, n_2^*. \tag{5}$$

The usual method that is employed to determine the amount adsorbed (and which leads to composite isotherms) is the following:

$$n_2^{\#} = (m^o - m)\,(n_1^o M_1/1000), \tag{6}$$

where $n_2^{\#}$ is the apparent number of moles of the solute adsorbed, n_1^o is the total number of moles of solvent added initially, M_1 is the molecular weight of the solvent, m^o is the molality of the original solution and m is the equilibrium molality. The molalities are defined such that

$$m^o = (n_2^o/n_1^o)\,(1000/M_1) \tag{7}$$

and

$$m = (n_2'/n_1')\,(1000/M_1). \tag{8}$$

We substitute the results of equations (4) and (5) into equation (8) and obtain

$$m = \left[\frac{n_2 - n_2^*}{n_1 + (A_2/A_1)\, n_2^*}\right] \frac{1000}{M_1}\,. \tag{9}$$

Substituting equations (7) and (9) into equation (6) we obtain

$$n_2^{\#} = \left[\frac{n_2^o\; 1000}{n_1^o\; M_1} - \frac{n_2 - n_2^*}{n_1 + (A_2/A_1)\, n_2^*}\left(\frac{1000}{M_1}\right)\right] \frac{n_1^o\; M_1}{1000}$$

$$= n_2^o - \frac{n_1^o\,(n_2 - n_2^*)}{n_1 + (A_2/A_1)\, n_2^*}$$

$$= \frac{n_2^o\, n_1 + n_2^o\,(A_2/A_1)\, n_2^* - n_1^o\, n_2 + n_1^o\, n_2^*}{n_1 + (A_2/A_1)\, n_2^*}\,.$$

Recognizing that $n_1 n_2^o = n_2 n_1^o$, from (3), and solving for n_2^* we have

$$n_2^* = \frac{n_1 \, n_2^\#}{n_1^o + (A_2/A_1)\,(n_2^o - n_2^\#)} \,. \tag{10}$$

If now we make the assumption that the original solution is very dilute in component 2, then the term $(A_2/A_1)\,(n_2^o - n_2^\#)$ becomes negligible compared with n_1^o, particularly if the solute is strongly adsorbed (i.e., $n_2^\# \longrightarrow n_2^o$). Then,

$$n_2^* = (n_1 \, n_2^\#)/n_1^o. \tag{11}$$

Since $0 < n_1/n_1^o < 1$, we see that $n_2^* < n_2^\#$, as was mentioned above. The ratio n_1/n_1^o may approach unity closely if enough solution volume is combined with the adsorbent. For example, suppose 5 milliliters of a dilute aqueous solution are added to one gram of an adsorbent having a surface area of 600 m^2 per gram. Assuming a molecular cross-sectional area for water of 10 Å^2, one may calculate that about 0.01 moles of water can be adsorbed as a monolayer on the adsorbent. The total number of moles of water introduced is approximately 5/18 or about 0.28 mole. Then, the ratio $n_1/n_1^o = (0.28 - 0.01)/0.28$ or 0.96. By increasing the ratio of solution volume to adsorbent weight the ratio n_1/n_1^o can be made to approach unity more closely, in which case $n_2^\#$ becomes a very good approximation for n_2^*. In the experimental results to be presented in a succeeding section, the isotherms are composite; but because the solutions employed were very dilute, the isotherms may be considered to approximate reasonably well the individual isotherms of the adsorbate, as shown above.

Several general equations for isotherms have been developed based upon theoretical models. The Langmuir equation was developed originally for adsorption of a gas as a monolayer (i.e., adsorption forces considered short-range only). It has been adapted for adsorption from solution. According to this model it is assumed that the rate of adsorption of the adsorbate is proportional to the concentration of the adsorbate in the bulk phase and to the fraction of the surface not covered by the adsorbate. The rate of desorption of the adsorbate is assumed proportional to the fraction of the surface covered by the adsorbate. At equilibrium the rate of adsorption equals the rate of desorption of the adsorbate. The resulting equation is well known.

$$x/m = \frac{a\,b\,c}{1 + a\,c}\,, \tag{12}$$

where x/m is the amount adsorbed per gram of adsorbent, c is the equilibrium concentration, and a and b are constants. This may be rearranged into the following form which yields linear isotherms for systems obeying the Langmuir equation:

$$\frac{c}{x/m} = \frac{1}{ab} + \frac{c}{b}\,. \tag{13}$$

The constants in the equation have some theoretical significance. According to Cassidy[11] the constant b refers to the amount of adsorbate which would saturate a unit surface with a monolayer. According to Adamson,* a is related to the heat of adsorption by the equation

$$a = a' \exp\left[\, q/(RT)\right]\,,$$

where q is the heat of adsorption.

---

*Adamson, A., Physical Chemistry of Surfaces, Interscience Publishers, Inc., New York, 1960.

From the form of equation (12) it is seen that at very low concentration levels the isotherm reduces to

$$x/m = a\,b\,c = k\,c\ . \qquad (14)$$

This result has also been obtained by Fu, Hansen, and Bartell[22] by combining the Gibbs adsorption equation

$$A\,d\,\phi = R\,T\,n_2^{s}\,d\ln c_2 \qquad (15)$$

and an equation of state for an ideal two-dimensional solution

$$A\,\phi = n_2^{s}\,R\,T\ , \qquad (16)$$

where ϕ is the spreading pressure, A is the surface area of the adsorbent, n_2^s is the total number of moles of component 2 at the surface, and c_2 is the bulk concentration of component 2. Assuming that specific adsorption does occur, for dilute solutions n_2^s may be considered identical to a term $A\Gamma_2$. Γ_2 is the surface excess and is defined as the excess of component 2 in the surface layer of unit area compared with the amount present in that quantity of the bulk solution which contains the same number of moles of component 1.[42] Equation (16) is differentiated with respect to ϕ and n_2^s to give

$$A\,d\,\phi = R\,T\,dn_2^{s}\ . \qquad (17)$$

Then, equating equations (15) and (17) one obtains after integration

$$n_2^{s} = k\,c_2 \qquad (18)$$

which is comparable to equation (14).

The Freundlich equation for isotherms is frequently applicable to adsorption from solutions. It is written as

$$x/m = k\ c^{1/n} \tag{19}$$

where k and n are constants. From the form of the equation it is apparent that, unlike the Langmuir isotherm, no limiting saturation value is obtained. Adamson* has stated that in an approximate way 'k' is a measure of the surface area of the solid, and 'n' a measure of the intensity of adsorption. The equation is essentially an empirical one, based on no theoretical model.

Kipling[42] has shown, however, that the Freundlich equation may be derived by combining an expression for the free energy of the surface with the Gibbs adsorption equation. But this derivation holds only for dilute solutions where $x/m = \Gamma_2$. The Gibbs equation can then be written as

$$x/m = \Gamma_2 = -\frac{d\sigma}{R\ T\ d\ln a_2} \tag{20}$$

where σ is the interfacial tension, and a_2 is the activity of the solute in the equilibrium bulk solution. It should be noted that ϕ, the two-dimensional spreading pressure employed in equation (15), is defined[33] as $\phi = \sigma_s - \sigma$, where σ_s is the surface tension of the clean surface and σ is the interfacial tension produced by the solution monolayer at equilibrium. Thus, since σ_s remains constant throughout the adsorption process, $d\phi = -d\sigma$. The free energy at the solid-solution interface is given by Kipling[42] as

$$\sigma = \sigma_1\ (1-\theta) + \sigma_2\ \theta \tag{21}$$

---

*Ibid.

where σ_1 and σ_2 are the free surface energies when the surface is in contact with pure solvent and pure solute, respectively, and θ is the fraction of the surface covered by the solute at equilibrium. So,

$$\theta = \frac{x/m}{(x/m)_m} \tag{22}$$

where $(x/m)_m$ is the maximum monolayer capacity. By substituting equation (22) into (21) and differentiating the result with respect to σ and x/m, one obtains an expression for $d\sigma$ which may be substituted into the Gibbs equation (20). The result is

$$x/m = \frac{1}{R\ T} \frac{(\sigma_1 - \sigma_2)}{(x/m)_m} \left[\frac{d(x/m)}{d\ln a_2} \right] . \tag{23}$$

Upon integration we obtain

$$\ln(x/m) = \frac{R\ T\ (x/m)_m}{\sigma_1 - \sigma_2} \ln a_2 + \ln k . \tag{24}$$

If we let $\frac{R\ T\ (x/m)_m}{\sigma_1 - \sigma_2}$ equal $1/n$, then $x/m = k\ a_2{}^{1/n}$.

Since for dilute solutions a_2 may be approximated by c_2 we have

$$x/m = k\ c_2{}^{1/n}$$

which is identical to equation (19).

The Gibbs adsorption equation has already been referred to (equation 20). Although it was originally derived with reference to the solution-vapor interface, the derivation may apply equally well to the solid-solution interface. The derivation has been presented by many authors.[75] One begins with the general expression for the differential Gibbs free energy of a system which includes the term σ dA. This is combined with an expression for the total differential of free energy. The result for a binary solution at constant temperature and pressure is an equation of the form

$$- d\sigma = \Gamma_1' d\mu_1 + \Gamma_2' d\mu_2$$

where Γ_1' and Γ_2' are the surface concentrations of component one and component two, and μ_1 and μ_2 are the chemical potentials of components one and two in the bulk solution, respectively. When the concept of surface excess, Γ_2, as defined on page 34, is employed it can be shown[42] that the above equation reduces to

$$\Gamma_2 = - \frac{d\sigma}{R\ T\ d\ln a_2}$$

as given in equation (20). This adsorption equation describes isotherms as a function of not only equilibrium concentration and amount adsorbed, but also the equilibrium interfacial tension. It defines the manner in which lowering of the surface free energy accompanies the adsorption process.

It may be of interest at this point to consider the relationship between the interfacial tension at the solid-solution interface and the surface tension at the solution-vapor interface. According to Young's equation[42]

$$\sigma_{LS} = \sigma_{SV} - \sigma_{LV} \cos \alpha, \tag{25}$$

where σ_{LS} and σ_{LV} are the surface tensions at the solution-solid and solution-vapor interfaces, respectively, σ_{SV} is the surface tension at the interface of vapor and 'clean' solid surface, and α is the contact angle at the solution-vapor interface. If we assume that the contact angle, α, is zero, and noting that σ_{SV} is a constant, we obtain upon differentiation

$$d\sigma_{LS} = - d\sigma_{LV} \tag{26}$$

Some attempts have been made to correlate the particular shape of experimental isotherms with the mechanism of adsorption. Giles, MacEwan, Nakhwa, and Smith[24] have grouped experimental solution isotherms into four classes on the basis of the shape of the initial portion of the curve. Then some conclusions as to the molecular orientations of adsorbate and degree of its relative affinity for the adsorbent have been drawn for each class of isotherm.

Thermodynamics of adsorption from solution

There has been recent interest in characterizing the thermodynamics of adsorption from solution. Beginning from statistical mechanical considerations, Everett[19,20] has developed equations describing thermodynamic relationships for adsorption from solution. Kipling[42] has presented a good review of the best thermodynamic treatments of adsorption from solution. Earlier developments of a theory of the thermodynamics of adsorption from solution have been presented by Thomas[85] and by Fu, Hansen, and Bartell.[22]

In the following development we will make use of contributions from the authors just mentioned, as applied to dilute solutions. We will be concerned with methods of determining $\Delta \bar{\bar{G}}^o$, $\Delta \bar{\bar{H}}^o$, and $\Delta \bar{\bar{S}}^o$ for a given system. The activity coefficient of the solute in the adsorbed phase will be discussed briefly. The derivation of a differential heat of adsorption will be presented. Then the influence of the solubility-temperature effect upon $\Delta\bar{H}$ and $\Delta\bar{S}$ as well as upon $\Delta\bar{H}^{\circ}$ and $\Delta\bar{S}^{\circ}$ will be discussed. Finally, the total free energy change involved in the adsorption process, together with the total enthalpy change will be considered.

1. Determination of $\Delta\bar{G}^{\circ}$, $\Delta\bar{H}^{\circ}$, and $\Delta\bar{S}^{\circ}$

Considering a system as a whole, the criterion for equilibrium is given by

$$\sum_i \mu_i \, dn_i = 0 \tag{27}$$

where μ_i is the partial molar free energy of component i, and n_i is the number of moles of i. Let us consider adsorption from a binary solution only. Then, one should recognize that $dn_i^s = - dn_i$, and that $dn_1 = - (A_2/A_1)\, dn_2$, where A_2 and A_1 represent the molar cross-sectional area at the surface of components 2 and 1, respectively. It follows then that equation (27) may take the following form (after Everett[19]):

$$\frac{\mu_1^s}{A_1} + \frac{\mu_2}{A_2} = \frac{\mu_1}{A_1} + \frac{\mu_2^s}{A_2}\,, \tag{28}$$

where μ_i is the chemical potential of the i^{th} component in the bulk solution, and μ_i^s is the chemical potential of the i^{th} component in the adsorbed phase. It may be noted that the factor $1/A_i$ has the dimensions of moles per unit area. In stating equation (28) as the overall condition for equilibrium it must be remembered that the condition

$$f_i = f_i^s$$

and so $$\mu_i = \mu_i^s \tag{29}$$

must hold for each component at equilibrium, where f_i and f_i^s are the fugacities of component i in the bulk phase and in the adsorbed phase, respectively.

In defining the chemical potential of the solute in the adsorbed phase (μ_2^s) we assume a model in which at very low levels of adsorption each solute molecule is adsorbed on the adsorbent surface singly. Each adsorbed solute molecule is surrounded on all sides (but the adsorbing surface) by only solvent molecules. Then, the model involves the assumption that at such low surface coverages by the solute a behavior analogous to Henry's Law behavior prevails. That is,

$$f_2^s = k'c_2^s \tag{30}$$

where f_2^s is the fugacity of the adsorbed solute, c_2^s is the concentration of the adsorbed solute in moles per 1000 grams of adsorbed solvent, and k' is a constant.

The chemical potentials of the solute and solvent are defined as follows. We will follow the convention throughout that component 1 refers to the solvent and component 2 to the solute. For the solvent in the bulk phase we have

$$\mu_1 = R\,T\,\ln f_1 + B(T).$$

and $$\mu_1^o = R\,T\,\ln f_1^o + B(T).$$

μ_1 and μ_1^o are the chemical potentials of the solvent at a given specified state and in the standard state, and f_1 and f_1^o are the fugacities of the solvent at a specified state and at the standard state. The standard fugacity of the solvent in the bulk phase is chosen such that

$$\lim_{X_1 \to 1} a_1/X_1 = \lim_{X_1 \to 1} f_1/f_1^{o}X_1 = 1.$$

We define the activity coefficient of the solvent in the bulk phase, γ_1, by the expression $\gamma_1 = a_1/X_1$, where a_1 is the activity of the solvent in the bulk phase and X_1 is its mole fraction. For the solvent which is adsorbed we have, following Everett[19]

$$\mu_1^{s} = R\,T\ln f_1^{s} - \sigma A_1$$

and $$\mu_1^{o,s} = R\,T\ln f_1^{o,s} - \sigma_1^{o} A_1$$

where μ_1^{s} is the chemical potential of the adsorbed solvent and f_1^{s} is its fugacity. The symbols σ and σ_1^{o} are the interfacial tensions, respectively, for a given equilibrium point and for the standard state of the solvent (i.e., with pure solvent wetting the surface). A_1 is the cross-sectional area which is covered by a monolayer consisting of one mole of pure solvent. It can be seen that at $X_1^{s} = 1$, $f_1^{s} = f_1^{o,s}$, where X_1^{s} is the mole fraction of the solvent in the adsorbed phase. In the case of the solute in the bulk phase we have

$$\mu_2 = R\,T\ln f_2 + C(T)$$

and $$\mu_2^{o} = R\,T\ln f_2^{o} + C(T).$$

We define γ_2 such that $\gamma_2 = a_2/c_2$. Here, f_2^{o} is defined such that

$$\lim_{c_2 \to 0} a_2/c_2 = \lim_{c_2 \to 0} f_2/f_2^{o}c_2 = 1,$$

where a_2 and c_2 represent the activity and the molality of the solute in the bulk phase. We see that f_2^{o} equals k, the Henry's Law constant, from the equation $f_2 = kc_2$, which holds only in the dilute limit. Considering the solute in the adsorbed phase we have, following Everett

$$\mu_2^s = R\,T\ln f_2^s - \sigma A_2$$

and $$\mu_2^{o,s} = R\,T\ln f_2^{o,s} - \sigma_2^o A_2.$$

We define γ_2^s such that $\gamma_2^s = a_2^s/c_2^s$. While Everett selected the standard state for the adsorbed solute as that in which the surface is in contact with pure component 2, we choose as standard state for the adsorbed solute a hypothetical one molal adsorbed layer, extrapolated from infinitely low surface coverages. So, we choose $f_2^{o,s}$ such that

$$\lim_{c_2^s \to 0} a_2^s/c_2^s = \lim_{c_2^s \to 0} f_2^s/(f_2^{o,s}c_2^s) = 1.$$

We, thus, are assuming a Henry's Law-type behavior at low surface coverages in accordance with equation (30), such that $f_2^{o,s} = k'$. σ_2^o equals the interfacial tension of the system (at the solid-solution interface) at the standard state for the adsorbed solute (i.e., when the amount of solute adsorbed is so slight that essentially pure solvent is adsorbed). Thus, we see that $\sigma_2^o \cong \sigma_1^o$.

Now we utilize the condition for equilibrium as stated in equation (28). Substituting into equation (28) the aforementioned expressions for chemical potentials we have

$$\frac{\mu_1^{o,s} + R\,T\ln a_1^s - (\sigma-\sigma_1^o)\,A_1}{A_1} + \frac{\mu_2^o + R\,T\ln a_2}{A_2}$$

$$= \frac{\mu_1^o + R\,T\ln a_1}{A_1} + \frac{\mu_2^{o,s} + R\,T\ln a_2^s - (\sigma-\sigma_2^o)\,A_2}{A_2}.$$

By substituting $\sigma_1^{\,o}$ for $\sigma_2^{\,o}$, and by rearrangement we come to the expression

$$A_2(\mu_1^{\,o,s}-\mu_1^{\,o}) - A_1(\mu_2^{\,o,s}-\mu_2^{\,o}) = R\ T\ \ln\left[(a_2^{\,s}/a_2)^{A_1}(a_1/a_1^{\,s})^{A_2}\right]$$

$$= R\ T\ \ln K_o \text{ (at equilibrium)},$$

where K_o is the thermodynamic equilibrium constant for the overall process. Because of the way we defined the standard states for component 1

$$\mu_1^{\,o,s} - \mu_1^{\,o} = 0,$$

and for initial solutions very dilute in the solute (component 2)

$$(a_1/a_1^{\,s})^{A_2} \approx 1.$$

Thus, we obtain

$$- A_1(\mu_2^{\,o,s}-\mu_2^{\,o}) = R\ T\ln(a_2^{\,s}/a_2)^{A_1}; \quad \text{and so}$$

$$- (\mu_2^{\,o,s}-\mu_2^{\,o}) = R\ T\ln(a_2^{\,s}/a_2) = R\ T\ln K_o. \qquad (31)$$

This expression can be shown to be identical to that obtained by Fu, Hansen, and Bartell,[22] who considered only the solute throughout. Their development follows.

At equilibrium $\mu_2 = \mu_2^{\,s}$.

They define $\mu_2^{\,s}$ such that $\mu_2^{\,s} = \mu_2^{\,o,s} + R\ T\ln a_2^{\,s}$.

Then $\mu_2^{\,o} + R\ T\ln a_2 = \mu_2^{\,o,s} + R\ T\ln a_2^{\,s}$

or $\mu_2^{\,o,s} - \mu_2^{\,o} = - R\ T\ln(a_2^{\,s}/a_2) = - R\ T\ln K_2$.

This is identical to equation (31). Thus, we see that K_2 (the thermodynamic equilibrium constant for the 2nd component alone) equals K_o (the thermodynamic equilibrium constant for the entire adsorption reaction) in the case of very dilute solutions.

From equation (31) we see that $\Delta \bar{G}^o = \mu_2^{o,s} - \mu_2^o = - R\,T\ln K_o$. In order to determine $\Delta \bar{G}^o$, the ratio a_2^s/a_2 must be known. The activities of the solute adsorbed on the solid cannot be measured directly. We can measure the ratio c_2^s/c_2 for any point on the isotherm. And we know by the way we defined γ_2^s and γ_2 that as the bulk solution concentration (or the amount adsorbed) approaches zero these activity coefficients approach one. Thus, we may say that

$$\lim_{c_2 \text{ or } c_2^s \to 0} (c_2^s/c_2) = a_2^s/a_2 = K_o,$$

where c_2^s and c_2 are the concentration of solute in the adsorbed phase and the bulk phase in moles per 1000 grams of solvent in their respective phase. By plotting c_2^s/c_2 versus c_2^s and extrapolating to zero c_2^s, one should be able to obtain a reliable value for K, and thence $\Delta \bar{G}^o$.

Then, $\Delta \bar{H}^o$ is obtained from the Van't Hoff equation

$$\frac{d\ln K_2}{dT} = \frac{\Delta \bar{H}^o}{R\,T^2}\,. \tag{32}$$

This equation may be integrated if one assumes that $\Delta \bar{H}^o$ remains substantially unchanged over the temperature range considered. $\Delta \bar{H}^o$ is defined by the expression, $\Delta \bar{H}^o = \bar{H}_2^{o,s} - \bar{H}_2^o$, where $\bar{H}_2^{o,s}$ is the partial molar enthalpy of the adsorbed solute in its standard state, and $\bar{H}_2^o$ is the partial molar enthalpy of the solute in the bulk phase in its standard state. After integration and rearrangement we obtain

$$\Delta \bar{H}^{o} = \frac{R\ T_1T_2}{T_2 - T_1} \ln (K_{T_2}/K_{T_1}) \tag{33}$$

where K_{T_2} and K_{T_1} are the equilibrium constants at the two temperatures T_2 and T_1. Thus, it is necessary to obtain an isotherm for a given system at two temperatures in order to determine $\Delta \bar{H}^{o}$. However, Bering and Serpinsky[6] have described a method for gas adsorption in which the heats and entropy changes associated with adsorption may be calculated from a single isotherm. This method requires that both the equation of the isotherm and the thermal coefficient of bulk expansion of the adsorbate be known. It is not known whether or not this method can be applied to solution isotherms.

Once $\Delta \bar{G}^{o}$ and $\Delta \bar{H}^{o}$ are known, $\Delta \bar{S}^{o}$ may be determined from the relationship

$$\Delta \bar{G}^{o} = \Delta \bar{H}^{o} - T \Delta \bar{S}^{o}. \tag{34}$$

Here $\Delta \bar{G}^{o}$ represents the average of the two $\Delta \bar{G}^{o}$ values at T_2 and T_1. T in equation (34) equals $(T_2 + T_1)/2$, where the units are degrees Kelvin. If isotherms at several temperatures have been obtained $\Delta \bar{S}^{o}$ may also be obtained from the relationship

$$\left(\frac{\partial \Delta \bar{G}^{o}}{\partial T}\right)_{P} = - \Delta \bar{S}^{o}. \tag{35}$$

It should be pointed out that correlation between $\Delta \bar{S}^{o}$ values obtained from equation (35) and those obtained from equation (34) does not necessarily verify the accuracy of the $\Delta \bar{S}^{o}$ values obtained. From a discussion by McGregor and Milićević[55] one may conclude that if the values of K at several experimental temperatures do not vary very much, there may be a linear correlation between the values of $\Delta \bar{H}^o$ and $\Delta \bar{S}^o$, where the former is determined from equation (33) and the latter from equation (35).

2. The activity coefficient of the solute in the adsorbed phase

From equation (31) we may immediately write an expression for $\gamma_2{}^s$, the activity coefficient of the solute in the adsorbed phase, following Fu, Hansen, and Bartell.[22]

$$K_2 = a_2{}^s/a_2 = (\gamma_2{}^s\ c_2{}^s)/a_2$$

Thus,

$$\gamma_2{}^s = K_2(a_2/c_2{}^s) \tag{36}$$

Assuming one can measure the activity of the solute in the bulk solution, or that a_2 can be approximated by c_2 for dilute solutions, we may obtain values for $\gamma_2{}^s$ at any equilibrium concentration. Fu, Hansen, and Bartell calculated values of $\gamma_2{}^s$ in this manner from data for the adsorption of butyric acid on graphite from aqueous solutions. They interpreted a change from positive to negative slope in curves obtained by plotting log $\gamma_2{}^s$ versus log $c_2{}^s$ as indicating that adsorption had advanced from monolayer adsorption to multilayer adsorption.

3. The differential heat of adsorption at constant interfacial tension

The isosteric heat of adsorption is defined as the differential heat of adsorption when the amount of adsorbate adsorbed is kept constant. It is calculated, for solution adsorption, by means of an equation analogous to the Clausius-Clapeyron equation.[85]

$$Q_{\Gamma} = - \frac{R\ T_1 T_2}{T_2 - T_1} \ln (a_{T_2}/a_{T_1})_{\Gamma} ,$$

where a_{T_2} and a_{T_1} are the equilibrium activities of the solute in the bulk phase at temperatures T_2 and T_1 at constant surface coverage (Γ). Then values of Q_{Γ} may be plotted against values of x/m to show the way in which Q_{Γ} varies with the extent of coverage. Hill[33] has clearly pointed out, however, that for the adsorption of vapor Q_{Γ} , the isosteric heat, does not represent the true difference in partial molar enthalpy of the adsorbate in the bulk and adsorbed phases. In his development he shows that Q_{Γ} equals $\Delta \bar{H}$ plus another term which includes the partial derivative $\left(\frac{\partial \phi}{\partial T}\right)_{\Gamma}$,

where ϕ is the two-dimensional spreading pressure, as previously defined. It is not easy to determine the values of $\left(\frac{\partial \phi}{\partial T}\right)_{\Gamma}$, so that the true differential enthalpy change, $\Delta \bar{H}$, can be determined. But he has been able to derive another form of the Clausius-Clapeyron type of equation which yields the values of $\Delta \bar{H}$ directly. His equation is the following:

$$\left(\frac{\partial \ln p}{\partial T}\right)_{\phi} = - \frac{\Delta \bar{H}}{R\ T^2} . \qquad (37)$$

These heats are found by plotting values of ϕ (obtained from a form of the Gibbs equation) versus p for two temperatures. Then values for p are taken for constant values of ϕ. In what follows I wish to derive an equation applicable to adsorption from dilute solutions which would be analogous to equation (37). In this case we will arbitrarily define

c_2 and c_2^s differently from the way we defined them before. We will let c_2 be the concentration of solute in the bulk phase in ug/ml of solvent, and c_2^s be the concentration of solute in the adsorbed phase in ug/ml of adsorbed solvent.

At equilibrium the fugacities of the solute in the bulk and adsorbed phases are equal.

$$f_2 = f_2^s$$

and so $$\ln f_2 = \ln f_2^s.$$

Let us consider the following functional relationships for $\ln f_2$ and $\ln f_2^s$:

$$\ln f_2 = g(T,P,c_2)$$

and $$\ln f_2^s = h(T,P,c_2^s, \sigma),$$

where σ is the interfacial tension at the solid-solution interface,* T is the absolute temperature, and P is the pressure. Then it follows that

$$d \ln f_2 = \left(\frac{\partial \ln f_2}{\partial T}\right)_{P,c_2} dT + \left(\frac{\partial \ln f_2}{\partial P}\right)_{T,c_2} dP + \left(\frac{\partial \ln f_2}{\partial c_2}\right)_{T,P} dc_2 \quad (38)$$

and

---

*It should be pointed out that while absolute values for σ cannot be determined, values for the change in the interfacial tension ($\Delta\sigma$) accompanying adsorption are obtainable from adsorption data by the use of the Gibbs adsorption equation. $\Delta\sigma$ is related to the commonly used concept of spreading pressure, ϕ, by the relation, $\Delta\sigma = - \phi$. ϕ was defined on page 35.

$$d \ln f_2^{s} = \left(\frac{\partial \ln f_2^{s}}{\partial T}\right)_{P,c_2^{s},\sigma} dT + \left(\frac{\partial \ln f_2^{s}}{\partial P}\right)_{T,c_2^{s},\sigma} dP$$

$$+ \left(\frac{\partial \ln f_2^{s}}{\partial c_2^{s}}\right)_{T,P,\sigma} dc_2^{s} + \left(\frac{\partial \ln f_2^{s}}{\partial \sigma}\right)_{T,P,c_2^{s}} d\sigma \qquad (39)$$

Now, as shown by Klotz[44]

$$\left(\frac{\partial \ln f_2}{\partial T}\right)_{P,c_2} = \frac{\bar{H}_2^{*} - \bar{H}_2}{R\,T^2}$$

and, so also $\left(\frac{\partial \ln f_2^{s}}{\partial T}\right)_{P,c_2^{s},\sigma} = \frac{\bar{H}_2^{*} - \bar{H}_2^{s}}{R\,T^2}$

where $\bar{H}_2^{*}$ is the partial molar heat content of the solute at zero pressure, $\bar{H}_2$ is the partial molar heat content of the solute in the bulk solution, and $\bar{H}_2^{s}$ is the partial molar heat content of the solute in the adsorbed phase. At very dilute concentrations we assume that Henry's Law applies to the bulk solution

$$f_2 = kc_2.$$

Therefore, $\ln f_2 = \ln c_2 + \ln k,$

and upon differentiation

$$d\ln f_2 = d\ln c_2.$$

Thus, $\left(\frac{\partial \ln f_2}{\partial c_2}\right)_{T,P} = \left(\frac{\partial \ln c_2}{\partial c_2}\right)_{T,P} = \frac{1}{c_2}.$

Then, $$\left(\frac{\partial \ln f_2}{\partial c_2}\right)_{T,P} dc_2 = \frac{dc_2}{c_2} = d\ln c_2.$$

We have defined c_2 such that

$$c_2 = (m_2/m_1)\,\rho_1,$$

where m_2 is the mass of solute in μg in the bulk solution, m_1 is the mass of solvent in grams in the bulk solution, and ρ_1 is the density of the solvent in the bulk solution at the mean temperature (of the two experimental temperatures, T_2 and T_1, which will appear in equation 41).

Then, $$\ln c_2 = \ln m_2 - \ln m_1 + \ln \rho_1$$

and $$d\ln c_2 = d\ln m_2 - d\ln m_1.$$

Thus, $$\left(\frac{\partial \ln f_2}{\partial c_2}\right)_{T,P} dc_2 = d\ln m_2 - d\ln m_1 = \frac{dm_2}{m_2} - \frac{dm_1}{m_1}.$$

In an entirely similar fashion we may treat the adsorbed phase, in which case we assume that

$$f_2^s = k' c_2^s$$

and, thus $$d\ln f_2^s = d\ln c_2^s.$$

Consequently, $$\left(\frac{\partial \ln f_2^s}{\partial c_2^s}\right)_{T,P,\sigma} = \frac{1}{c_2^s}$$

and $$\left(\frac{\partial \ln f_2^s}{\partial c_2^s}\right)_{T,P,\sigma} dc_2^s = d\ln c_2^s.$$

Further, we defined c_2^s such that

$$c_2^s = (m_2^s/m_1^s)\rho_1^s,$$

where m_2^s is the mass of solute in the adsorbed phase in μg, m_1^s is the total mass of solvent in the adsorbed phase in grams, and ρ_1^s is the density of the adsorbed solvent at the mean temperature. Then we obtain

$$\ln c_2^s = \ln m_2^s - \ln m_1^s + \ln \rho_1^s,$$

and $$d\ln c_2^s = d\ln m_2^s - d\ln m_1^s.$$

Thus, $$\left(\frac{\partial \ln f_2^s}{\partial c_2^s}\right)_{T,P,\sigma} dc_2^s = d\ln m_2^s - d\ln m_1^s = \frac{dm_2^s}{m_2^s} - \frac{dm_1^s}{m_1^s}.$$

At this point we may equate equations (38) and (39) because of the equilibrium condition. We will consider that the adsorption process occurs at constant pressure, and, in addition, we will maintain the condition that $d\sigma = 0$. Therefore, we have

$$\left(\frac{\bar{H}_2^* - \bar{H}_2}{R\ T^2}\right) dT + \frac{dm_2}{m_2} - \frac{dm_1}{m_1} = \left(\frac{\bar{H}_2^* - \bar{H}_2^s}{R\ T^2}\right) dT + \frac{dm_2^s}{m_2^s} - \frac{dm_1^s}{m_1^s} \qquad (40)$$

Rearranging, we obtain

$$\left(\frac{\bar{H}_2^s - \bar{H}_2}{R\ T^2}\right) dT = \left(\frac{dm_2^s}{m_2^s} - \frac{dm_2}{m_2}\right) - \left(\frac{dm_1^s}{m_1^s} - \frac{dm_1}{m_1}\right).$$

We define $\Delta \bar{H}_\sigma = \bar{H}_2^s - \bar{H}_2$, because $\Delta \bar{H}_\sigma$ is the quantity representing the differential heat of adsorption when σ is held constant. Recognizing that $dm_2^s = -dm_2$, and that $dm_1^s = -dm_1$, we see that

$$\frac{\Delta \bar{H}\sigma}{R\ T^2}\ dT = -\ dm_2\left(\frac{m_2 + m_2{}^s}{m_2{}^s m_2}\right) + dm_1\left(\frac{m_1 + m_1{}^s}{m_1{}^s m_1}\right).$$

Now, $m_2 + m_2{}^s = m_2{}^o$, and $m_1 + m_1{}^s = m_1{}^o$, where $m_2{}^o$ and $m_1{}^o$ represent the total mass in μg and in grams in the system of the solute and solvent, respectively. Thus,

$$\frac{\Delta \bar{H}\sigma}{R\ T^2}\ dT = -\ dm_2\left[\frac{m_2{}^o}{(m_2{}^o - m_2)m_2}\right] + dm_1\left[\frac{m_1{}^o}{(m_1{}^o - m_1)m_1}\right].$$

Upon integration between the limits of T_1 and T_2, we obtain

$$\frac{\Delta \bar{H}_\sigma(T_2 - T_1)}{R\ T_2T_1} = \ln\left(\frac{m_2{}^o - m_2}{m_2}\right)\Bigg|_{m_2 \text{ at } T_1}^{m_2 \text{ at } T_2} - \ln\left(\frac{m_1{}^o - m_1}{m_1}\right)\Bigg|_{m_1 \text{ at } T_1}^{m_1 \text{ at } T_2}$$

And since $m_i{}^o - m_i = m_i{}^s$, the result is

$$\frac{\Delta \bar{H}_\sigma(T_2 - T_1)}{R\ T_2T_1} = \ln\left[\frac{(m_2{}^s/m_2)_{T_2}}{(m_2{}^s/m_2)_{T_1}}\right] - \ln\left[\frac{(m_1{}^s/m_1)_{T_2}}{(m_1{}^s/m_1)_{T_1}}\right].$$

Considering that we are dealing with dilute solutions we may assume for levels of adsorption considerably less than a full monolayer coverage by the solute, that

$$\frac{(m_1{}^s/m_1)_{T_2}}{(m_1{}^s/m_1)_{T_1}} \approx 1$$

Thus, the final result for dilute solutions is

$$\Delta \bar{H}_\sigma = \frac{R\ T_1T_2}{T_2 - T_1}\ln\left[\frac{(m_2{}^s/m_2)_{T_2}}{(m_2{}^s/m_2)_{T_1}}\right] \qquad (41)$$

To use equation (41) several values of $\Delta\sigma$ must be calculated from the Gibbs equation (for dilute solutions) for each isotherm. This form of the Gibbs equation is given by equation (58). Then, by plotting these values versus corresponding values for m_2^s/m_2, one can obtain values for m_2^s/m_2 at two temperatures at a constant change in interfacial tension. With these pairs of values for m_2^s/m_2 one can easily solve for $\Delta \bar{H}\sigma$. From the derivation of equation (41) it is seen that $\Delta \bar{H}\sigma$ is equal to the difference between the partial molar enthalpy of the solute in the adsorbed phase and that of the solute in the bulk phase at equilibrium. The partial molar entropy change at equilibrium ($\Delta \bar{S}\sigma$) may be easily determined once $\Delta \bar{H}\sigma$ is known, from the relation $\Delta \bar{H}\sigma = T \Delta \bar{S}\sigma$, because $\Delta \bar{G} = 0$ at any point on the isotherm.

It is interesting to note from the preceding development that if Γ (here, c_2^s) had been held constant, but σ permitted to vary (as is done in obtaining isosteric heats), one would not obtain a definition of Q from which the enthalpy and entropy changes could be readily calculated using ordinary experimental data. This is because the expression given by equation (40) would then include the term $(\partial \ln f_2^s/\partial\sigma)_{T,P,c_2^s}\, d\sigma$, while the term $(dm_2^s/m_2^s - dm_1^s/m_1^s)$ would be deleted.

4. The effect of the solubility-temperature relationship upon changes of thermodynamic properties in adsorption

The relationship between the solubility of a solute and its adsorbability has been studied by several workers.[31,46,47] Some workers report they have been unable to discover any relationship between solubility and adsorbability.[31] Frequently, however, for a given solvent-adsorbent system definite correlations between extent of adsorption and solubility have been obtained for a homologous series of solutes. Kurlyandskaya and Martynov[47] reported a linear inverse relationship between log N and log Γ for $CuCl_2$, $FeCl_3$, and $AlCl_3$ in a $SiCl_4$-silica gel system and for a series of straight-chain fatty acids and alcohols in a water-activated carbon system. Here, N represents the solubility of the solute in the solvent employed, and Γ refers to the slope of the linear section of the isotherm.

But our concern here is with the effect of the solubility limit upon the thermodynamics of adsorption from solution. The principle involved is that the fugacity of a given solute at a constant concentration in solution will assume different values depending on the particular solvent employed and the temperature. The influence of the solvent here depends on the solute having different solubilities in the solvents employed. If the solute has the same solubility limit in two separate solvents its fugacity in each should be identical for equal concentrations. Temperature exercises an effect because the solubility limit of a solute in solution changes with temperature. Thus, the chemical potential of a solute in solution, also, is seen to depend at least in part upon the solubility of the solute as affected by the particular solvent and by the temperature.

Kipling[42] has stated that the reduced concentration (c_2/c_o) is a measure of the activity of the solute at a given concentration (c_2), where c_o is the solubility of the solute in the given solvent. If we replace the activity of the solute in solution by reduced concentration in our expression for the chemical potential of the solute in the bulk solution we obtain

$$\mu_2 = \mu_2^o + R\,T \ln(c_2/c_o) \tag{42}$$

But it is difficult to know whether one would be justified in equating this expression with that for μ_2^s, so that an expression for $\Delta \bar{G}^o$ (similar to equation 31) could be obtained. Such an expression for $\Delta \bar{G}^o$ would presumably be preferable to that obtained by assuming that

$$\mu_2 = \mu_2^o + R\ T\ \ln c_2 \tag{42a}$$

which is often used for dilute solutions. In other words, particularly in the case of solutes which are only sparingly soluble, c_2/c_o is a better approximation of a than is c_2. However, if one were to use equation (42) to find $\Delta \bar{G}^o$ it would seem most correct to equate it with an expression for μ_2^s of the following form:

$$\mu_2^s = \mu_2^{o,s} + R\ T\ \ln(c_2^s/c_o),$$

where c_2^s/c_o is the reduced surface concentration and c_o the solubility of the solute in the bulk solution. But, if this were done the resulting $\Delta \bar{G}^o$ would be identical to that defined by equation (31). Thus, let us retain our definition of $\Delta \bar{G}^o$ as given in equation (31). And we will look for the way in which the concept of reduced concentration can lead to values for $\Delta \bar{H}^o$ and $\Delta \bar{H}$ from which the solubility effect has been eliminated.

Kurlyandskaya and Martynov[47] have related the differential heat of solution (Q_s) and the differential heat of adsorption (Q_a) by defining a quantity Q', the differential heat of the hypothetical solid-adsorbent transition. Accordingly,

$$Q_a = Q' - Q_s. \tag{43}$$

Q' is a heat of adsorption which, unlike Q_a, is independent of the temperature-solubility relationship. For example, let us assume we have a system in which the solubility of the solute increases with temperature ($Q_s > 0$) and the degree of adsorption of the solute decreases with temperature ($Q_a < 0$). Then Q' will be positive if $|Q_s| > |Q_a|$ and negative if $|Q_s| < |Q_a|$.

We may identify Q_a, Q_s and Q' with $\Delta \bar{H}_\sigma$, $\Delta \bar{H}_s$, and $\Delta \bar{H}'$, respectively. $\Delta \bar{H}_\sigma$ is the differential heat of adsorption at constant change in interfacial tension and was defined previously as

$$\Delta \bar{H}_\sigma = \bar{H}_2^s - \bar{H}_2 \tag{44}$$

where $\bar{H}_2$ and $\bar{H}_2^s$ are the partial molar enthalpies of the solute in the bulk phase and in the adsorbed phase, respectively. Now $\Delta \bar{H}_s$ is defined as the change in the partial molar heat content of the solute accompanying solution.

$$\Delta \bar{H}_s = \bar{H}_2 - \bar{H}_s \tag{45}$$

where $\bar{H}_s$ is the molar enthalpy of the pure undissolved solute. By adding equations (44) and (45) we obtain

$$\Delta \bar{H}' = \bar{H}_2^s - \bar{H}_s$$

which corresponds with the definition of Q'.

Now by plotting isotherms at several temperatures, first as x/m versus c_2, and then as x/m versus c_2/c_o one can perceive qualitatively the relative magnitude of $\Delta \bar{H}_\sigma$ and $\Delta \bar{H}'$.

$\Delta \bar{H}'$ can be calculated by means of a modification of equation (41). In place of m_2 we substitute m_2/m_o (comparable to c_2/c_o) where m_o is the total mass of solute which the given solution volume will hold at saturation at the given temperature. Thus, we have

$$\Delta \bar{H}' = \frac{R\ T_1T_2}{T_2 - T_1} \ln \frac{\left[(m_2{}^s/m_2)\ m_o \right]_{T_2}}{\left[(m_2{}^s/m_2)\ m_o \right]_{T_1}} \qquad (46)$$

From equation (46) it can be shown that

$$\Delta \bar{H}' = \frac{R\ T_1T_2}{T_2 - T_1} \ln \left[\frac{(m_2{}^s/m_2)_{T_2}}{(m_2{}^s/m_2)_{T_1}} \right] + \frac{R\ T_1T_2}{T_2 - T_1} \ln \left[\frac{(m_o)_{T_2}}{(m_o)_{T_1}} \right]$$

The last term on the right-hand side is equal to $\Delta \bar{H}_s$ for a dissolved solute in a solution obeying Henry's Law in equilibrium with undissolved solute.[44] The first term on the right-hand side is just $\Delta \bar{H}_\sigma$. Thus, we see that the expression on the right-hand side of equation (46) is correct for determining $\Delta \bar{H}'$.

Similarly $\Delta \bar{H}^o$ (the change in the standard enthalpy due to adsorption) can be corrected so that the effect of solubility changes with temperature is eliminated. Equation (33) is modified by adding on the right-hand side the term

$$\frac{R\ T_1T_2}{T_2 - T_1} \ln \left[\frac{(c_o)_{T_2}}{(c_o)_{T_1}} \right].$$

This gives

$$\Delta \bar{H}^{o\prime} = \frac{R\ T_1T_2}{T_2 - T_1} \ln \left[\frac{(K\ c_o)_{T_2}}{(K\ c_o)_{T_1}} \right], \qquad (47)$$

where $\Delta \bar{H}^{o\prime}$ is the change in the standard enthalpy accompanying adsorption in which the effect of solubility changes with temperature has been removed. The values of standard entropy changes, calculated from $\Delta \bar{H}^{o\prime}$ and from $\Delta \bar{G}^o$, should also be independent of solubility-temperature effects.

5. Free energy change involved in the adsorption process

Thomas[85] has analyzed the components of the total free energy change in the process of adsorption from solution. For our purposes we will make certain modifications of his treatment. Let us consider the change in the total free energy that occurs from time zero at the instant when the solution is combined with the adsorbent, until the time when equilibrium is attained. Then, the total free energy change is given by

$$\Delta G = \Delta G^B + \Delta G^a \qquad (48)$$

where ΔG^B is the change in free energy of the solution due to the lowering of the bulk concentration and ΔG^a is the change in the free energy of the solution-solid interface (due to adsorption).

An expression for ΔG^B may be written immediately,

$$\Delta G^B = n_2^o R T \ln(a_e/a_i), \qquad (49)$$

where n_2^o is the total number of moles of solute added initially, a_i is the activity of the solute in the initial solution, and a_e the activity of the solute in the solution at equilibrium. Then, for ΔG^a Thomas[85] employs a form of the Gibbs adsorption equation, applicable for dilute solutions only.

$$\Delta G^a = - R T \int_o^{a_e} n_2{}^s \, d\ln a_e, \qquad (50)$$

where $n_2{}^s$ is the total number of moles of solute adsorbed on the adsorbent at equilibrium and a_e is as defined for the previous equation. Thomas also includes, in addition to ΔG^a and ΔG^B, another term, ΔG^s, representing the free surface energy change, which he defines in a manner identical to $\Delta\ G^a$ in equation (50). But it is difficult to see why this term is required, since the change in the surface tension or interfacial energy is completely taken care of by equation (50). And it is difficult to understand, assuming the adsorbent surface to be essentially inert, how the free energy of the surface of the adsorbent (apart from the adsorbed film) would change significantly, or at all, due to the adsorption process.

Thus, we conclude that the expression for Δ G is given by

$$\Delta G = n_2^o R T \ln(a_e/a_i) - R T \int_0^{a_e} n_2^s \, d\ln a_e \qquad (51)$$

This represents the total free energy change in a system due to adsorption within the limits described.

From values for Δ G obtained for identical systems at several temperatures, the values for the total change in the entropy of a system due to adsorption may be obtained from the relationship

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = - \Delta S. \qquad (52)$$

The chord-area method may be employed to obtain values for the partial derivative. Once Δ S is known at a given temperature Δ H may be determined from Δ S and from Δ G values at the same temperature. The value of Δ H so obtained would be the true integral heat of adsorption in which the heats of adsorption of the solute and desorption of the solvent would be included as well as the heat of dilution of the bulk solution. This is in contrast to the differential heat of adsorption ($\Delta \bar{H}_\sigma$) which was defined above. In the case of the latter quantity only the difference in the heat content of solute between adsorbed and bulk phases at equilibrium is involved.

In the following sections, the experimental design and methods, the results of the initial adsorption experiments, and the results of the isotherm studies will be presented and discussed in that order. The application of the theory of the thermodynamics of adsorption from solution just discussed will be presented in the section concerning the isotherm studies.

EXPERIMENTAL DESIGN AND METHODS

Purpose of study

The aim of the present study was to elucidate the behavior of the two BHC isomers (gamma- and beta-) in soils under controlled laboratory conditions. The writer desired to study the extent of their adsorption as well as their possible decomposition in solution-solid systems for several types of porous adsorbents and several solvents, including water. In particular, it was the purpose to ascertain, by employing sensitive methods of analysis, the nature of adsorption and decomposition of the isomers in solutions of very low concentrations, such as can be encountered in the field. Another goal of this study was to determine the energetics of adsorption of these compounds for differing systems, so that the strength of adsorption and reversibility of adsorption could be estimated. This involved a consideration of the affect of temperature upon the adsorption of the BHC isomers. Finally the writer desired to study how differing electrical properties of non-ionic stereoisomers affect the extent and energy of their adsorption. (The dipole moment of γ-BHC has been shown to be about 2.8 debye units compared to 0 debye units for the β-isomer.)

Materials

The untagged crystalline γ-BHC employed in the experiments was purchased from the J. T. Baker Chemical Company and certified to be 99-100% gamma-isomer with a melting point of 112-114°C. Untagged crystalline β-BHC was obtained from the City Chemical Corporation, New York, with a guaranteed purity of 95 percent. Radioactive gamma- and beta-isomers were obtained from the Nuclear-Chicago Corporation as C^{14}, uniform-labeled compounds supplied in benzene solutions. The radiochemical purity for both isomers was determined by the supplier to be 98% or higher by thin-layer chromatography. The specific activities of the radiochemicals were certified to be 111 microcuries/mg. for the γ-isomer, and 124 microcuries/mg. for the β-isomer.

Solvents were obtained from several suppliers. The benzene employed was reagent grade, A.C.S., Baker and Adamson quality, having the following properties: maximum boiling range of 0.5°C, thiophene content of 0.001%, and water content of 0.02%. The hexane used was nanograde hexane produced by the Mallinckrodt Chemical Works. It consists of a mixture of isomers with the formula, C_6H_{14}. Its density at 25°C was given as 0.687, and its boiling range as 4.0°C. Ethanol was obtained as 200-proof ethyl alcohol from the Commercial Solvents Corporation, Agnew, California.

Several adsorbents, including soils, clays, exchange resins, silica gel, and alumina, were utilized for the initial adsorption studies, but only four were chosen for obtaining isotherms. Surface samples (0-12") of Venado clay were obtained at the site where this soil series was established. It is an alluvial soil found in a California coastal mountain valley and formed from outwash from hills high in serpentine. Consequently, it naturally contains a high percentage of Mg^{++} on the cation exchange complex. The top soil in the field has a pH of about 7.5 and the surface contains grass roots. A partial mechanical analysis of the top soil of Venado clay revealed that about 45% (by oven-dry weight) consisted of particles less than 0.2 micron in diameter, 46% in the range 0.2 to 20 microns, and 3% greater than 20 microns (coarse silt and fine sand). The remainder (about 6 percent) consisted of organic matter. In the < 0.2 micron fraction, 85-95% was estimated by x-ray diffraction analysis to be montmorillonite, with the remainder probably serpentine. In the 0.2 to 2.0 micron range the primary mineral evident was chlorite (75-85%) along with serpentine. The 2.0 to 20 micron fraction was shown by x-ray analysis to consist of the same components present in the 0.2 to 2.0 micron range with the addition of some quartz and feldspar. Thus, the amount of montmorillonite in Venado clay may be estimated to fall in the range 38-43% by oven-dry weight, with chlorite comprising about 35-40% of the total weight. Assuming specific surface areas of 800 m^2/gm for montmorillonite and for the organic matter, and about 80 m^2/gm for the chlorite, these ranges of percentage composition yield a value for specific surface of the soil which corresponds closely with the value obtained by the ethylene glycol retention method.

Surface samples of Columbia silt loam, Oakley sand, and Staten peaty muck were also obtained. Both Columbia silt loam and Oakley sand were formed from stream deposits of mixed sedimentary and igneous materials. Columbia silt loam is a pale brown, somewhat micaceous, neutral soil. Oakley sand is a brown, single-grained sand usually containing abundant fine roots. The pH range of the surface soil is 5.5 to 6.0. Staten peaty muck is a high-organic soil developed from tule-reed peat in the delta of the Sacramento river. The pH of the surface soil is 5.5 to 6.0. In the field the surface horizon of Staten peaty muck contains 40-50% organic matter consisting of dark-gray, loose, partly-decomposed material.

Samples of Ca- and Na- Wyoming bentonite and Ca- and Na-kaolinite were obtained from Mr. Ralph Riggs of this department. The samples of Ca- and Na-bentonite and of Ca-kaolinite were of the particle size range 0.2 to 1.0 micron, effective diameter. The Na-kaolinite contained by weight two-thirds of the particles of a size greater than one micron, and one-third between 0.2 and 1.0 microns. A small sample of nontronite obtained from Dr. Lynn Whittig was saturated with sodium by stirring in an aqueous solution of 1.5N NaOAc followed by repeated washing with distilled water. The sample was air-dried and ground to less than 1.0 mm. with a porcelain mortar and pestle.

The exchange resins employed consisted of 100-200 mesh Dowex 50W-X8, in the H^+ form as the cation exchange resin, and 100-200 mesh Dowex 1-X8 in the Cl^- form as the anion exchange resin.

Silica gel (100-200 mesh) was obtained from the Fisher Chemical Company. It was specified as a Fisher certified reagent meeting ASTM D-1319-61T.

Fisher-certified neutral alumina with a Brockman activity of 1 was obtained from the Fisher Chemical Company. It was specified to have a pH of 8.15 with a size range of 80-200 mesh. A similar but more basic alumina (pH = 10.0) was obtained from Van Waters and Rogers, Inc., having a size range identical to the neutral alumina. Magnesium hydroxide was prepared by the writer by combining aqueous solutions of reagent grade NaOH and $MgCl_2$, followed by filtering, washing, air-drying, and oven-drying at 110°C.

Soil samples were prepared by air-drying, followed by crushing by means of a copper cylinder so that all particles passed through a 2mm sieve. The soil was then transferred to Buchner funnels in which the soil was subjected to continued leaching with 1.0N or 2.0N $Ca(OAc)_2$ $\left[\text{or } Mg(OAc)_2 \text{ in the case of one sample of Venado clay}\right]$.

Complete Ca-saturation (or Mg-saturation) of the soil was determined by analyzing the leachate by flame spectrophotometry. As soon as the concentration of the leachate came to within 2-3% of that of the original leaching solution with respect to the saturating cation, leaching with distilled water was begun. Leaching with distilled water was continued until the concentration of the leachate with respect to the saturating cation was reduced to a constant low level (0.8 to 2.5 milliequivalents/liter). During the Ca-saturation of one sample of Venado clay even after prolonged leaching with 1.0N $Ca(OAc)_2$ the Mg^{++} concentration level in the leachate never became lower than 5 meq./liter. After completion of the distilled water leaching, the soils were air-dried, ground to less than 1.0 mm. with a porcelain mortar and pestle, and oven-dried on aluminum foil at 105-110°C for 24 hours. The soils were stored in air-tight bottles which also had been heated at 105-110°C during the oven-drying of the soils. The bentonite, kaolinite, and nontronite samples were similarly oven-dried and stored.

One sample of Venado clay was pretreated with NaOAc (pH 5.0) and digested several times with 30% H_2O_2 in order to remove most of the organic matter. The treatment was in accordance with the method described by Jackson.[36] After the digestion by H_2O_2 the sample was leached with pH 5.0 NaOAc and then with distilled water. Finally the sample was saturated with Ca^{++} as described in the previous paragraph.

For a few of the adsorbents special determinations were made to ascertain their acidity, cation exchange capacity, percent carbon, and specific surface area. Values for pH were obtained from readings on a Corning pH meter of a slurry consisting of 10.0 grams of adsorbent in 200 ml of distilled water. Cation exchange capacity was determined according to the method of Schollenberger and Simon[77] with a few modifications. Twenty-gram samples of the adsorbents were leached with 400 ml of aqueous 1.0N NH_4OAc solution. This was followed by leaching with 95% ethanol. Then steam distillation of the entire soil sample was performed in pyrex Kjeldahl flasks (not copper flasks) until essentially all the ammonium ions had been driven off the soil as ammonia into flasks containing saturated boric acid solution. Titration of the ammonia-containing solutions with H_2SO_4 directly yielded values for the cation exchange capacity. Percent carbon content was determined by total combustion in a combustion train (as described in Methods of Soil Analysis, No. 9 in the Agronomy Series, p. 1367, American Society of Agronomy, Inc., Madison, Wisconsin, 1965). Dextrose was used as the standard reference material. Surface areas were determined according to the ethylene glycol method described by Bower and Gschwend.[7] The only deviations from their method were that no special H_2O_2 treatment was performed and that in the case of soils or clays the adsorbent was not converted to a hydrogen-form but was tested in its Ca-saturated state. The results of these determinations are summarized in table 8.

The surface area obtained for silica gel at first appears to be excessively high. Dyne and Sagert[15] report a surface area for silica gel (50-60 mesh) of 710 ± 60 $m^2/gm.$, calculated by the B.E.T. equation using N_2 as the adsorbate. In view of this, and considering the smaller particle size of the silica gel used in the present study (100-200 mesh), 890 m^2/gm may not be an unreasonable value for its surface area. The values obtained for the total and external surface

Table 8

Characteristics of Selected Adsorbents

Adsorbent	pH	Cation exchange capacity (meq/100 gm)	Percent carbon (of oven-dry weight)	Total surface area (m^2/gm)	External surface area (m^2/gm)
Ca-Staten peaty muck	6.6	54	11.9	2.3×10^2	-
Ca-Venado clay	8.5	48	3.1	4.2×10^2	1.3×10^2
H_2O_2-treated Ca-Venado clay	*	*	1.2	4.1×10^2	1.3×10^2
Ca-Columbia silt loam	7.5	14	1.1	*	*
Ca-Bentonite	8.3	80	0.08	8.1×10^2	6.9×10^2
Silica gel	4.4	*	*	8.9×10^2	-

* Indicates no determination was made.

areas for Ca-bentonite compare closely with those obtained by Bower and Gschwend[7] for Ca-Wyoming bentonite. The latter authors obtained a much lower external surface area for H-bentonite (72.3 m^2/gm) than for Ca-bentonite. This difference they found difficult to explain.

If one applies a factor of 1.9[ƒ] (ratio of the weight of total organic matter to the weight of carbon) to the percent carbon obtained for Staten peaty muck, one obtains a value of 22.7% organic matter.

[ƒ] This factor was suggested by Broadbent to give an approximate value for the percent organic matter in surface soils if the percent carbon is known. (Broadbent, F., "The Soil Organic Fraction," Advances in Agronomy 5:153-183, 1953)

As mentioned before, 40-50% organic matter is normally found in the surface layer of this soil. It is understandable that 17-27% organic matter may have been lost from the soil during the base saturation process and oven-drying. A comparison of values for the percent carbon in the case of untreated and H_2O_2-treated Venado clay shows that the H_2O_2 treatment removed a little less than two-thirds of the organic matter present in this soil.

Experimental procedure and methods

The experiments were designed so as to permit the determination of the amount of solute adsorbed at equilibrium as well as the extent of any possible decomposition of solute accompanying adsorption. To achieve this, solutions were prepared with a small amount of C^{14} uniform-labeled compound with the remainder made up with the normal non-radioactive isomer. Then, analysis of the equilibrium solution was performed both by liquid scintillation counting and by electron-capture gas chromatography. Decomposition was indicated when the concentration of adsorbate in solution as determined by gas chromatography was significantly less than the concentration as determined by radioisotope counting. If essentially no decomposition was demonstrated, the amount of solute adsorbed was determined indirectly from the difference between the concentration of the equilibrium and initial solutions. In the early initial adsorption studies liquid scintillation analysis was also performed directly on a portion of the adsorbent from the equilibrium solution. This was referred to as the 'solid series.' About 0.10 gram of adsorbent was quickly transferred from the equilibrium solution to a weighed liquid scintillation vial. After weighing, the vial and contents were counted. A vial containing 0.10 grams of untreated adsorbent in pure liquid scintillation solution served as the blank. By subtraction of the calculated net counts per minute (cpm) due to the small amount of equilibrium solution accompanying the adsorbent portion, the net cpm due to the compound adsorbed on the solid was obtained.

All sampling and dilution operations performed in these experiments were done volumetrically. All pipettes were rinsed with benzene and with ethyl alcohol immediately after use. Volumetric flasks which had contained solutions of BHC were rinsed with benzene and with ethyl alcohol prior to washing.

1. Preparation of solutions

All solutions were prepared so as to contain a constant concentration of radiochemical (5 microcuries/liter) as C^{14}-labeled γ-BHC or β-BHC. This produced a net count of 10,000 to 14,000 cpm for two ml of solution by liquid scintillation counting. In the case of the benzene solutions the radioactive aliquot to add to the solution flask was taken directly from the original benzene solution from the supplier, after an appropriate dilution. For nanograde hexane solutions, an aliquot containing the proper number of microcuries was evaporated to dryness and then taken up in nanograde hexane and washed into the solution flask. For the ethanol and distilled water solutions, the benzene solutions containing the radiochemical were evaporated to dryness under a gentle nitrogen stream. Just as soon as evaporation of the benzene was complete the precipitated radioisomer was washed into the solution flask with 5 ml of 200-proof ethyl alcohol. Since all the aqueous solutions were made up in one-liter volumetric flasks, this meant that the 'aqueous' solutions actually contained 0.5% EtOH, by volume.

The remainder of γ-BHC (or β-BHC) required to make the solution up to the desired concentration was added as the non-radioactive compound. For lindane solutions the appropriate amount of γ-BHC was weighed out on a Mettler Type H16 balance and then washed into the solution flask with the appropriate solvent. For aqueous γ-BHC solutions shaking by hand and magnetic stirring were carried out for three to four days to insure complete solution. For the β-BHC aqueous solutions it was found necessary to prepare a saturated aqueous solution by stirring excess β-BHC crystals in water on a magnetic stirrer for several days. Then following filtration of the saturated solution through a 4-6 micron fritted-glass filter, approproate volumes of this solution were transferred to the several flasks to obtain the desired final concentrations. All solutions were stored in the dark either in glass-stoppered volumetric flasks or in glass-stoppered reagent bottles. For the isotherm experiments, 12-20 hours prior to the introduction of the solutions into the experimental Erlenmeyer flasks, the solution bottles were placed in the constant temperature bath set at the temperature desired for the experiment.

The saturated aqueous β-BHC solution was analyzed by gas chromatography after extraction into hexane. It was found that some degree of isomerization had occurred in the water. (Four peaks of nearly the same retention time as that of the β-isomer appeared.) It was estimated that the β-isomer comprised at least 90% of all the BHC isomers present. Also, since at a dilution of 50:1 no peaks besides that for the β-isomer appeared, the writer felt justified in proceeding with the experiments and making use of this solution.

For determining isotherms in aqueous γ-BHC solutions, five solutions of the following concentrations were prepared: 0.056, 0.50, 1.0, 2.0, and 5.0 μg/ml. For isotherms of β-BHC in aqueous solutions, the solution concentrations employed were 0.075, 0.18, 0.38, 0.53, and 0.65 μg/ml. The magnitude of the concentrations of these latter solutions was determined by electron-capture gas chromatography using a prepared solution of β-BHC in nanograde hexane as standard. For determining isotherms for γ-BHC in nanograde hexane, eight solutions of the following concentrations were prepared: 0.10, 0.50, 1.0, 3.0, 10.0, 50.0, 200.0, and 500.0 μg/ml.

2. Procedure in equilibrium studies

The procedure to be described below applies to almost all the adsorption experiments. Any important exceptions will be noted in the presentation of the results.

Five grams of oven-dried adsorbent were weighed into a 125-ml glass-stoppered Erlenmeyer flask. (In the case of many of the initial adsorption studies ten grams of adsorbent were used.) Weighing was carried out on a type K7 Mettler balance having an accuracy of ± 0.02 grams. For all the isotherm studies, following the weighing operation, the flasks with stoppers off were placed in an oven for 36 hours at 110°C in the case of nanograde hexane solutions, and 15 hours at 60°C in the case of aqueous solutions. After the heat treatment, 25 ml of the appropriate solution was added by pipette to each flask. There were two replicates for each concentration level for each adsorbent.

In addition, adsorbent blanks were included. Further, duplicate flasks containing 25 ml of solution (but lacking any adsorbent) for each concentration were included. These served as standard blanks and were the references used in measuring the extent of adsorption in the other flasks at equilibrium. The standard blanks were treated in exactly the same way as the flasks containing both solution and adsorbent.

As soon as the solutions had been transferred to the flasks, the flask tops were covered with polyethylene bags secured by rubber bands so as to prevent the bath water from leaking down into the flasks. Then the flasks were placed immediately in the bath and secured. The constant-temperature water bath used was supplied by the American Instrument Company (catalog number 4-8605). A shaking mechanism supplied by the same company had been installed in the bath. Temperature variation within the bath itself and within the time period of the experiment did not exceed 0.05°C.

After the flasks were placed in the bath they were shaken at a moderate rate for a period of 20 hours. Then they were allowed to remain at rest for an additional 50 hours before sampling. Adsorption experiments performed, in which the writer varied the time the flasks remained in the bath before sampling, indicated that equilibrium had been essentially established after a total of 70 hours in the bath.

3. Sampling methods

The sampling method employed depended upon the particular solvent in use. For benzene and hexane solutions no suspensions with the adsorbents occurred. By X-ray diffraction analysis it was estimated that 0.25% or less of the clay adsorbents could be considered to be in suspension in these organic solvents. Further, analysis of samples obtained directly (without centrifugation) and of those obtained following centrifugation indicated no significant difference. Therefore, sampling from the benzene and hexane solutions was done directly. Ten ml of the supernatant were withdrawn from each flask (in place in the bath) and placed in 25-ml glass-stoppered test tubes. These were stoppered, shaken, and stored in the dark to await analysis.

Suspension of clay and soil adsorbents definitely occurred in the case of aqueous solutions. Thus, centrifugation was required prior to sampling. Centrifugation was carried out on all aqueous solutions as well as ethanol solutions. Standard blanks and adsorbent blanks were also centrifuged in the same manner. The flasks were removed from the bath six or eight at a time. The suspensions were swirled and quickly poured into 50-ml stainless steel centrifuge tubes. The tubes were immediately placed in the centrifuge which was set at the same temperature as the water bath. The suspensions were centrifuged at 10,000 rpm for 20 minutes. After measuring the temperature of the supernatant, 10 ml of the supernatant were transferred to a glass-stoppered test tube. The solution samples in the test tubes were stored in the dark.

The centrifuge employed was a Servall refrigerated-automatic centrifuge. It was, unfortunately, not possible to maintain close temperature control in the centrifuge. Average temperature deviation from the desired temperature was about 0.5°C with a maximum deviation of 1.0°C.

4. Extraction methods

Some preliminary experiments pertaining to extraction procedures were carried out. It was found that lindane completely codistilled with water when aqueous solutions of lindane were evaporated to dryness, the 'residue' immediately taken up in xylene for gas chromatographic analysis. It was, thus, found imperative to extract all aqueous solutions of γ- and β-BHC directly with an organic solvent in order to analyze by gas chromatography. (If aqueous solutions are used directly in such analysis, the chromatographic column and detector may be permanently harmed, and the analysis is hindered by the presence of the large peaks resulting.) Tests indicated that extraction efficiencies were the same whether extraction was performed in a separatory funnel or in a 25-ml glass-stoppered test tube. Since the upper (organic) phase was the one desired for analysis, it was decided to use the simpler method of extracting in the test tubes.

Only a slight increase in extraction efficiency was observed in employing two or three extractions compared to one. It was decided, therefore, to extract the aqueous solutions only once. Slightly higher extraction efficiencies were observed using benzene when the test tube was shaken vigorously for three-fourths of a minute compared to relatively easy inversions for 1 1/2 minutes. The method involving relatively easy inversions for 1 1/2 minutes was chosen because in this case there was much less chance for stable emulsions to develop. Stable emulsions were troublesome in preparing the solutions for analysis, and were encountered fairly often when the hard shaking method was employed. Finally, the solvent chosen for extraction was nanograde hexane because it produced no interfering peaks in gas chromatographic analysis, while the benzene and xylene employed occasionally did. Further, when a saturated aqueous solution of lindane was extracted with benzene and with nanograde hexane, in duplicate, the average concentration of the hexane solutions determined by gas chromatographic analysis was more than three times that of the benzene solutions.

In extraction, 10.0 ml of nanograde hexane were pipetted on top of the 10.0 ml of aqueous solution in each glass-stoppered test tube. Then, each tube was inverted back and forth briskly for 1 1/2 minutes. This was performed within an hour after completion of the sampling from the centrifuge tubes. After inverting the tubes, they were placed in the dark for 12-48 hours before withdrawal of the solutions for analysis.

The partition coefficient of β-BHC between nanograde hexane and water was estimated by liquid scintillation counting. One milliliter each of the hexane extract of two standard blank aqueous solutions of β-BHC (0.42 and 0.46 μg/ml) were counted. At the same time one milliliter of the aqueous phase after extraction was counted for both solutions. The results are shown in table 9.

Table 9

Estimation of the Partition Coefficient for two β-BHC solutions

Conc. of nanograde hexane extract by G. C. (μg/ml)	Net cpm of hexane phase per ml after extraction	Net cpm of aqueous phase per ml after extraction	Partition coefficient (hexane: water)
0.42	5,660	32	180
0.46	4,440	31	140

The partition coefficient of γ-BHC between nanograde hexane and water may reasonably be assumed to be of the same order of magnitude for the same concentration range.

5. Quantitative analysis of equilibrium solutions

Because the response of the electron-capture detector is not linear over a wide concentration range, it was necessary to dilute samples to a concentration which would fall within the linear range of the instrument. The linear range was < 0.20 μg/ml for γ-BHC, and < 0.40 μg/ml for β-BHC. Dilutions were performed by removing to volumetric flasks the required aliquot from the upper hexane extract (in the case of aqueous solutions) or directly from the 10-ml portion sampled from the equilibrium solution (in the case of the other solvents). In all cases, except in earlier experiments with benzene solutions, nanograde hexane was used as the solvent in making dilutions. From the same solution portion from which dilutions for gas chromatographic analysis were made, two milliliters, undiluted, were transferred to a liquid scintillation vial containing 15 ml of liquid scintillation solution. After shaking the vials, and allowing them to come to temperature inside the spectrometer, counting was carried out.

Counting was done in a Tri-Carb Liquid Scintillation Spectrometer, series 314E, manufactured by the Packard Instrument Company. In counting these C^{14}-labeled compounds a tap setting of 4.40 (voltage = 9.35 volts) was chosen because it was found by trial and error to yield a maximum S^2/B ratio, where S is the total cpm of a C^{14} sample, and B is the total cpm of a blank sample. The A-B channel was set for the range, 1-8, while the C-D channel was set for the range, 4.5

to 10, so as to read about one-half of the counts of the A-B channel. This was to facilitate observation of changes in the ratio (A-B cpm)/(C-D cpm) due to quenching.

A set of 'matched' vials were used for counting. That is, the total counts per minute of any vial with 15 ml of pure scintillation solution did not exceed, or fall below, the mean for the set by more than 10%. For each sample the average of five ten-minute counts was taken to find the gross cpm. Subtraction of the average cpm for the blank vials from the average gross cpm yielded the average net cpm for each sample. The number of net counts per minute was assumed to be linearly related to the concentration of BHC isomer in solution. This involved the assumption that the radioactive isomer behaved in a fashion identical to that of the non-radioactive isomer.

The counting efficiency is defined as the ratio of cpm obtained to the number of actual disintegrations occurring per minute. The latter quantity is calculated from the radioactivity of the solution in millicuries. The counting efficiency for C^{14}-labeled lindane was calculated as 48% for liquid scintillation counting.

The liquid scintillation solution was formulated by mixing the following: 865 ml of ethanol, 1370 ml of 1,4-dioxane, 1370 ml of toluene, 180.0 grams of naphthalene, 18.00 grams of PPO, and 0.36 grams of POPOP.

The percent deviation of ten-minute counts from the mean of five such counts varied from 0.1 - 0.6% for high radioactive concentrations (6,000 to 15,000 cpm) to 1.5 - 4.0% for low radioactive concentrations (50 to 250 cpm). The percent deviation of the average net cpm between replicates in the adsorption experiments was calculated on the basis of the initial concentration. For almost every experiment the percent deviation between replicates was less than 1.5%, and commonly less than 0.8%. When nanograde hexane was used as the solvent, the deviation between duplicates was higher than for the other solvents by a factor of two or more. A satisfactory reason for this could not be found. In almost every case gas chromatographic analysis showed a higher deviation between replicates than that obtained by liquid scintillation counting.

Gas chromatographic analysis was performed with an Aerograph Hy-Fi, Model 600-B gas chromatograph equipped with an electron-capture detector. A Honeywell Brown Electronik recorder, 1 millivolt range, was employed in conjunction with the gas chromatograph. The recorder was equipped with a disc integrator which measured the relative area under the solute peaks. The column usually used was a five-foot by 1/8-inch pyrex column packed with 60/80 Chromosorb W and having as the liquid phase 5% Dow 11. Oven temperatures were kept at $180^{\circ} \pm 3^{\circ}C$. The pressure of the nitrogen carrier gas was maintained constant for each set of determinations, somewhere in the range 25 to 35 psi.

Injections were made with a 10 μl Hamilton syringe. After injection the syringe was held in the injection port for four seconds -- long enough for all the sample except about 0.1 μl to be volatilized off onto the column. The net volume of solution injected was determined by subtracting the volume remaining in the syringe from the initial volume before injection. For each replicate and standard, four separate injections were made consecutively. Appropriate standard solutions were injected between every four to six experimental samples.

The proper volume of solution to inject was selected so that the height of the resulting γ-BHC or β-BHC peak was less than one-third of the pen deflection indicating the magnitude of the standing current. In this range the peak areas were assured to be linear with concentration. The retention times for β-BHC and γ-BHC on the column at 25 psi were 2.77 minutes and 3.10 minutes, respectively. A diluted sample of pure C^{14}-labeled γ-BHC in nanograde hexane was analyzed by gas chromatography. A value was obtained for its concentration which was approximately 25% less than that calculated from the Chicago-Nuclear specifications. When a diluted sample of pure C^{14}-labeled β-BHC was analyzed by gas chromatography, the concentration was determined to be about 7% higher than that calculated from the specifications for its specific activity.

The areas of the G.C. peaks were determined with the aid of the disc integrator. Care was taken to adjust the sensitivity control of the electrometer so that each peak began at the base line. In cases when the peak did not terminate on the base line there was a discrepancy between the area indicated by the disc integrator and the true area. In this case a correction was made by extrapolating the disc integrator line after the peak was concluded, back to the point vertically opposite to the point where the peak began. Half of this vertical distance was either added or subtracted from the indicated area for the peak, depending on whether the peak terminated below or above the base line. Each peak area so obtained was divided by the number of microliters injected to give an area/µl value. Peak areas for each sample were obtained by averaging the peak area/µl values for the four injections. In the initial adsorption studies concentrations were determined by averaging the concentration value obtained by peak areas with that obtained by total peak height. Later, it was concluded that equally reliable values could be obtained using peak areas alone. Thus, the latter method was employed for the G.C. analyses in the isotherm studies. Concentrations were determined by relating the average peak area/µl to that of a known standard solution.

There was considerable deviation in peak area/ul values between injections of the same sample. In one test with four lindane solutions, each injected 4 to 5 times, it was found that the percent average deviation from the mean area/µl value (of the 4 to 5 injections) ranged from 1.0% to 4.3%.

6. Method of calculation

In the case of liquid scintillation counting the concentration of the equilibrium solution in each case was determined by multiplying the known concentration of the appropriate standard (in µg/ml) by the ratio of the net cpm for the sample to the net cpm of the standard. The total amount adsorbed in micrograms (x) was calculated as follows

$$x = (c_s - c)V, \tag{53}$$

where c_s and c are the final concentrations of the standard blank solution and the equilibrium solution, respectively, and V is the total solution volume added initially. In cases when the temperature in the centrifuge exceeded 0.5°C above or below the desired temperature, density corrections were applied to the equilibrium concentration values before the above calculation was performed. The amount adsorbed per gram of adsorbent (x/m) was calculated by dividing x by the number of grams of adsorbent. When equation (53) was applied to concentrations obtained from G.C. analysis, the value x was interpreted as the total mass in micrograms of γ-BHC or β-BHC missing from solution. When this value was definitely greater than that obtained from liquid scintillation counting, the difference was taken as the number of micrograms in solution which had decomposed. Although the evidence of such decomposition was, thus, apparent, it was not possible to determine whether the adsorbed molecules consisted of the pure undecomposed BHC isomers or whether they were made up, in part, of the decomposed products.

Uncertainties in the data obtained were estimated by combining an estimated value for experimental error with an estimate of the uncertainty due to the limitations of the analytical instruments employed. The average relative uncertainties in the values for equilibrium concentration (c) and the amount adsorbed per gram (x/m) as calculated from L.S. analysis were estimated as 1% and 3%, respectively. The corresponding maximum percent uncertainty for these values was estimated to be 2% and 7%, respectively. The average percent uncertainty in c and x/m as calculated from G.C. analysis was estimated as 3% and 6%, respectively, with the corresponding maximum percent uncertainty being 5 and 12%.

7. Determination of solubilities

Saturated solubilities of γ-BHC and β-BHC in aqueous solutions at 20°C and 30°C were determined. To correspond to the aqueous solutions used in the equilibrium studies, 0.5% ethanol by volume was added to each aqueous solution. Further, the saturated solubility of γ-BHC in nanograde hexane at 10° and 20°C was determined. Powdered

BHC isomer crystals were added in excess to 400 milliliters of solvent in glass-stoppered one-liter bottles. The bottles were placed in the constant-temperature water bath. The bottles remained in the bath for 68 hours during which time shaking was done intermittently. After this period, sampling was performed by transferring 30-40 ml from the upper part of the solution to a glass-stoppered test tube. During this process the aliquots were filtered through a fritted glass filter (4-6 micron). In the case of saturated aqueous solutions, extractions into nanograde hexane were performed, as described previously. Following appropriate dilutions, analysis was carried out by gas chromatography.

Unexpectedly, some isomerization occurred in γ-BHC aqueous solutions. And, there was a degree of isomerization of β-BHC in aqueous solution not observed in the saturated solution which had been prepared for the adsorption studies. No isomerization occurred in the case of the saturated hexane solutions of γ-BHC.

While no isomerization apparently occurred during the adsorption studies, the saturated aqueous solution of γ-BHC showed the presence of a compound with a retention time 0.81 times that of lindane. This apparent isomer (possibly α-) had a concentration roughly one-fiftn to one-fourth that of the γ-isomer.

The saturated aqueous solution of β-BHC exhibited three peaks having retention times, relative to lindane, of 0.810, 0.905, and 1.095. All three peaks had roughly the same area. While the middle peak represents the β-isomer, the first and last peaks are thought to represent the α- and δ-isomers, respectively.

Figures 3 and 4 represent the chromatograms for the diluted extract from the saturated aqueous solution of γ-BHC and β-BHC,

FIGURE 3

GAS CHROMATOGRAM
SATURATED AQUEOUS γ-BHC
EXTRACTED INTO HEXANE
50:1 DILUTION

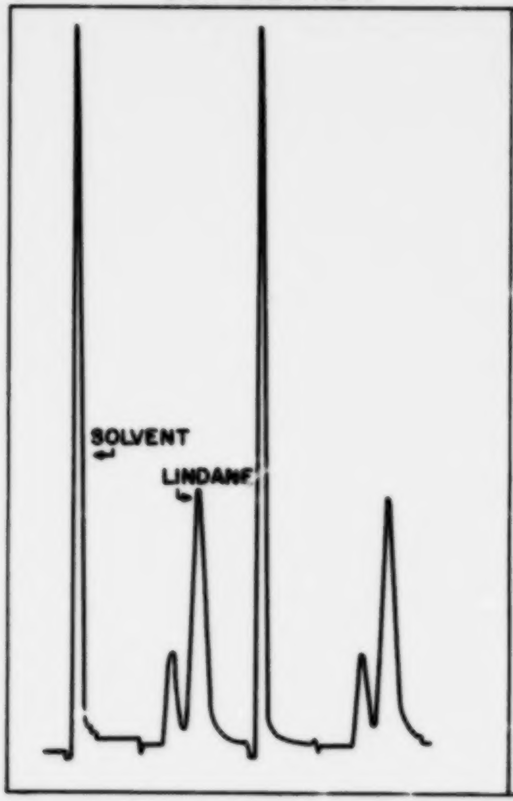
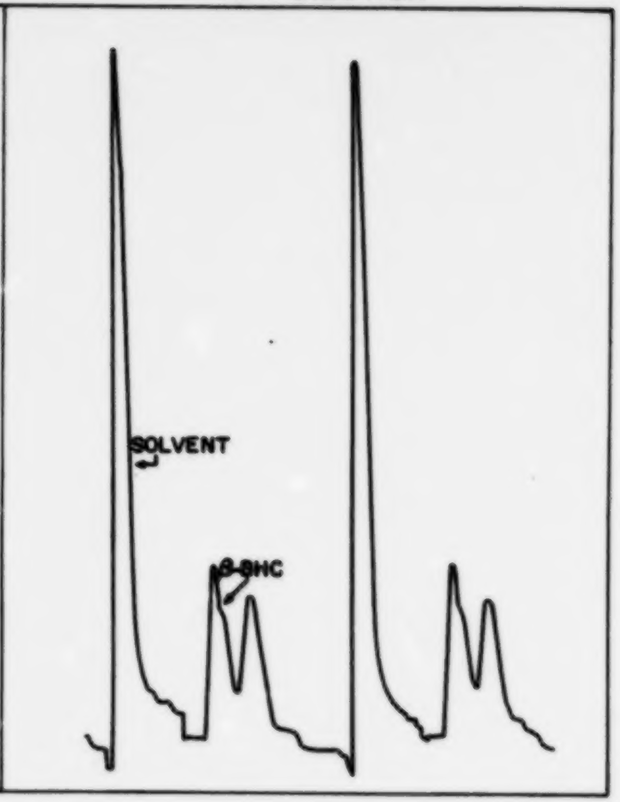


FIGURE 4

GAS CHROMATOGRAM
SATURATED AQUEOUS β-BHC
EXTRACTED INTO HEXANE
10:1 DILUTION



respectively. Figures 5 and 6 represent the chromatograms of the standard hexane solutions of γ-BHC and β-BHC, respectively.

The reason for the occurrence of isomerization of the two isomers in the determination of their solubility in water may well be related to the nature of the aqueous saturated state. Isomerization was not encountered in initial adsorption studies nor in the isotherm studies in which aqueous solutions of concentrations definitely lower than saturation were employed.

In order to obtain some values for the solubilities of the β- and γ-isomers in such an aqueous system (containing 0.5% EtOH) it was necessary to measure the areas of the peaks for all the isomers. Then, the writer had to assume that this total area represented the concentration of the single isomer concerned. At best this provided only a reasonable estimate of the saturated solubility of the isomer in such a system.

The results of these solubility determinations are reported in table 10. One should note that the solubilities of γ-BHC in this aqueous system at 20° and 30°C are about 2.0 and 1.44 times higher, respectively, than those reported by Riggs* for a maximum diameter of 5.0 microns. (Values are read off a curve plotted from his four temperature points.) This increased solubility could well be due to the small amount of ethanol in the system employed by the present writer.

---

* Refer to table 7, page 24.

FIGURE 5

GAS CHROMATOGRAM
STANDARD SOLUTION OF
γ-BHC IN HEXANE

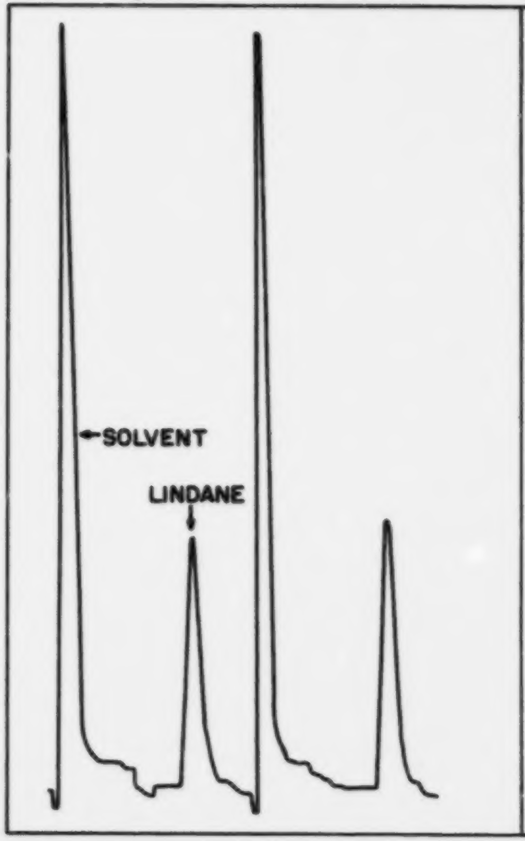


FIGURE 6

GAS CHROMATOGRAM
STANDARD SOLUTION OF
β-BHC IN HEXANE

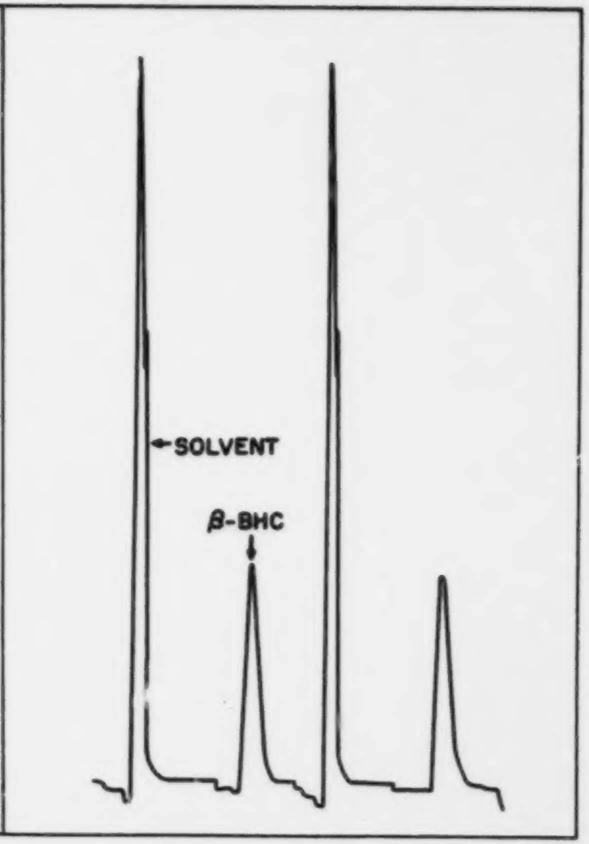


Table 10

Solubilities of β- and γ-BHC

Isomer	Solvent	Temperature (^{o}C)	Conc. of saturated solution
γ-	distilled water with 0.5% EtOH	20	8.5 µg/ml
		30	13.1 µg/ml
γ-	nanograde hexane	10	9.76 mg/ml
		20	13.97 mg/ml
β-	distilled water with 0.5% EtOH	20	2.7 µg/ml
		30	3.6 µg/ml

RESULTS AND DISCUSSION

Initial adsorption experiments

All the initial adsorption studies were performed using lindane. Its isomer, β-BHC, was not employed until the isotherm experiments were undertaken. The initial experiments were conducted to enable the writer to choose the most effective experimental procedure and methods in obtaining isotherms. They involved the evaluation of the effect in adsorption studies of certain variables, such as heat pre-treatment of adsorbents, centrifugation just prior to sampling, time, adsorbent mass, solution volume, and type of cation on the exchange complex. Any exception to the methods outlined in the experimental section will be noted.

1. Influence of heat pre-treatment of adsorbents

Ten grams of Ca-Venado clay were weighed into glass-stoppered Erlenmeyer flasks. There were three 72-hour heat treatments (with stoppers off) prior to the addition of a benzene solution containing 5 μg/ml γ-BHC. The results of the liquid scintillation analysis are shown in table 11.

Table 11

Effect of Heat Pre-treatment of Adsorbents upon Adsorption of γ-BHC from Benzene Solutions at 25°C

Temp. of pre-treatment (°C)	Equil. conc. (ug/ml)	% Deviation between duplicates	x/m (μg adsorbed per gram of adsorbent)
25	5.05	0.16	-0.12
111	4.60	0.47	1.00
224	4.49	0.75	1.27

It is apparent from Table 11 that positive adsorption of lindane from benzene solutions onto Venado clay is possible only if the adsorbent has been preheated above room temperature. The reason for this may be linked to the loss of interlayer water at the higher temperatures. This water may be adsorbed on sites which have more affinity for the lindane molecules than for the benzene molecules. It seems that benzene can compete more effectively than lindane for sites on which there were no water molecules prior to the heat treatment. Because of this finding all adsorbents in subsequent experiments involving benzene or hexane solutions were heated at 110°C for 36-72 hours after being weighed into glass-stoppered Erlenmeyer flasks.

The effects of varying heat treatments of adsorbents (25° and 110°C) for 73 hours prior to the introduction of an aqueous solution (or ethanol solution) containing 5 μg/ml γ-BHC were also studied. Table 12 summarizes the results of the liquid scintillation analysis.

Table 12

Effect of Heat Pre-treatment of Adsorbents upon Adsorption from Solutions at 20°C

μg adsorbed (x) per gm adsorbent (m)

	Solvent			
	water		ethanol	
Pre-treatment temperature	25°C	110°C	25°C	110°C
Adsorbent				
Ca-bentonite	11.5	10.3	-	-0.60
Ca-Venado clay	22.7	22.5	-0.35	-0.30
Ca-Staten peaty muck	24.7	24.6	2.20	3.70

As seen in Table 12, for ethanol and aqueous solutions there is no clear effect of the heat treatment before the addition of the solution. Only with Ca-bentonite in water and with Ca-Staten peaty muck in ethanol can there be seen obvious differences between the two temperature treatments. The data for these two cases indicate that while there tends to be an increase of positive adsorption of γ-BHC from ethanol when the pre-treatment temperature increased from 25° to 110°C, the reverse is true for aqueous solutions. The same explanation as advanced for benzene solutions may apply to ethanol solutions. It is not apparent why the extent of adsorption dropped with Ca-bentonite in water as the pre-treatment temperature increased. It could be related to changes in the clay structure upon heating which might act to reduce the number of sites for which lindane has affinity. It was decided that for the isotherm studies all the adsorbents would be heated for 15 hours at 60°C prior to the addition of aqueous solutions, so as to make the moisture content of all the adsorbents more or less constant.

2. The effect of centrifugation of organic solutions

Two experiments were performed to determine whether or not centrifugation was required for obtaining samples from systems with organic solvents. In both solutions tested, benzene and nanograde hexane, the concentration of γ-BHC in the centrifuged sample was somewhat higher than the concentration of the solution sampled directly from the glass-stoppered Erlenmeyer flasks. Thus, it seems clear that there was no effect of high apparent concentration due to suspended adsorbent particles on which lindane molecules were adsorbed.

Table 13 shows the results of obtaining 10-ml samples of hexane solution directly, compared to obtaining them following centrifugation (for 20 minutes at 10,000 rpm) of the entire solid-solution mass. The initial hexane solution had a concentration of 100.0 µg/ml. Values reported are from the liquid scintillation analysis.

Table 13

Comparison of Centrifugation versus Direct Sampling of a Hexane Solution of γ-BHC at 20°C

Adsorbent	Sampling method	Average equil. conc. (µg/ml)	Deviation between duplicates (% of initial solution)
Ca-Venado clay	direct	47.1	0.2
	after centrifugation	48.8	0.1
Ca-Staten peaty muck	direct	90.9	0.1
	after centrifugation	92.1	0.6

Table 14 shows the results of analyzing several portions of the equilibrium supernatant solution from a benzene system with and without centrifugation. The initial solution concentration was 5.0 µg/ml and the adsorbent was Ca-Venado clay. In this case no heat treatment was given the adsorbent before solution addition.

Table 14

Effect of Method of Obtaining Sample Aliquot of Benzene Solution at 25°C

Method of obtaining aliquot in the order samples were obtained	Equil. conc. (μg/ml)	% deviation between duplicates
A. one ml directly from flask	4.97	2.2
B. 10 ml directly from flask, shaken & 1 ml used for analysis	5.03	0.7
C. one ml from supernatant after centrifugation of solution B	5.07	0.9
D. one ml from supernatant after centrifuging remaining soln. in flask	5.06	0.5

The slight increase in concentration of the equilibrium solution following centrifugation as shown in Tables 13 and 14 may indicate a slight lack of homogeneity in the solution of the adsorption flask. That is, the data indicate a slightly lower concentration of the upper portion of the equilibrium solution compared to that obtained for the solution adjacent to the adsorbent. It was decided that by withdrawing a 10-ml aliquot from a 25-ml volume of an organic solution in the adsorption flask, the resulting value would be reasonably representative of the entire equilibrium solution. Ca-Venado clay in hexane solution showed the maximum deviation (3.6%) between the concentration of a 10-ml volume obtained directly and that obtained after centrifugation of the entire mass.

3. Direct measurement of adsorption - 'solid series'

In several of the initial adsorption experiments a 'solid series' was included in the liquid scintillation analysis in an attempt to measure the amount of lindane adsorbed directly. This method was described in the experimental section. The values obtained by this direct measurement were almost invariably larger than those obtained from the measurement of the equilibrium solution. The higher apparent adsorption found with the 'solid series' is assumed to be due to the concentrating of the benzene solution which accompanied the ~0.10 gram of adsorbent, during its transfer to the liquid scintillation vial. Such concentration effects would doubtless have been less with less volatile solvents, such as water. But, unfortunately, the writer did not have the time to apply this method to aqueous solutions. The method was discontinued primarily because the percent deviation between duplicates was so high, as is shown in Table 15. This table summarizes the results of an experiment to determine the effects of varying the adsorbent mass upon the apparent adsorption per gram. The higher adsorption values for the solid series compared to that for the indirect determination ('liquid series') are seen in all but one instance. In this experiment 20 ml of solution were added rather than 25.

Table 15

Effect of the Mass of Venado Clay upon the Apparent Amount Adsorbed per gram from Benzene Solutions at 25°C (L.S. analysis)

Mass of oven-dry Ca-Venado clay (gm.)	Initial Solution Concentration							
	5 µg/ml				50 µg/ml			
	'liquid' series		'solid' series		'liquid' series		'solid' series	
	dev.*	x/m (µg/gm)	dev.	x/m (µg/gm)	dev.	x/m (µg/gm)	dev.	x/m (µg/gm)
1.0	0.3	0.36	40.0	0.95	0.4	7.60	-	6.84
5.0	0.2	0.80	3.7	1.27	1.1	5.20	42.8	19.2
10.0	0.2	1.08	15.7	1.60	0.8	7.64	21.3	14.2
15.0	3.1	0.85	-	1.33	2.0	7.48	13.7	12.4

* 'dev.' refers to the % deviation between duplicates.

4. Influence of adsorbent mass and the solution volume upon adsorption per gram

If we ignore the solid series values in Table 15, we see that there is some variation in the x/m values calculated from the equilibrium solution concentration, but that the relation to the mass of adsorbent is not clear. One should expect to obtain the highest values for the amount adsorbed per gram of adsorbent for the lowest mass of adsorbent because changes in adsorbent mass inevitably affect the equilibrium position. For example, in order to obtain the same x/m value for 5.0 grams as was obtained for 10.0 grams of adsorbent, a higher solution concentration, and, thus, a higher fugacity of the solute in the bulk phase result. But since this fugacity would then be greater than that for the solute on the adsorbent, a somewhat greater degree of adsorption would be brought about until equilibrium is achieved. In addition, higher x/m values with decreasing adsorbent mass might be expected to occur because the solution would presumably have more free access to all the pores of the adsorbent the less the amount of adsorbent present. This did not appear to be true for adsorption from the solution with an initial concentration of 5.0 µg/ml, as seen in Table 15. Yet, adsorption 'efficiency' (measured as x/m) did decrease when the mass of adsorbent increased from 10 to 15 grams. This held true for both solutions and for both the 'liquid' and the 'solid' series. In another experiment little difference was observed in the amount of lindane 'adsorbed' per gram from a 100 µg/ml benzene solution on 5.0 and 10.0 grams of Na-bentonite (-1.82µg/gm and -1.92 µg/gm, respectively). In the case of such negative adsorption, however, the influence of the mass of adsorbent might be less than when the solute is positively adsorbed.

Definite increased adsorption 'efficiencies' were observed for the adsorption of lindane from 100 µg/ml nanograde hexane solutions when the mass of Venado clay and Staten peaty muck was decreased from 10.0 to 5.0 grams. This is shown in Table 16. The smaller increase in x/m values for the muck compared to Venado clay when the adsorbent weight was decreased from 10.0 to 5.0 grams may be due to the higher natural porosity and greater percentage of larger pores of the muck compared to the clay. It was decided to employ 5.0 grams of adsorbent per flask for all the isotherm studies.

Table 16

Effect of Mass of Adsorbents upon Adsorption of Lindane from Nanograde Hexane Solutions (100.0 µg/ml)

Adsorbent	Mass of Adsorbent	x/m (ug/gm)
Ca-Venado clay	5.0	265
	10.0	166
Ca- Staten peaty muck	5.0	45.7
	10.0	38.8

The influence of varying the solution volume was observed in one experiment. Table 17 shows the affect of changing the initial volume of an aqueous solution of lindane (5 µg/ml) from 20 to 25 ml when in contact with 5.0 grams of Ca-Venado clay. It is obvious that a lower amount will be adsorbed at equilibrium from a smaller solution volume,

Table 17

Effect of Initial Solution Volume upon the Amount Adsorbed at 20.0°C

Solution volume (ml)	Equil. conc. (μg/ml) c	Dev.*	x/m (ug/gm)	$\frac{x/m}{c}$
20	0.373	0.2	18.5	49.6
25	0.460	0.3	22.7	49.4

* 'Dev.' is the deviation between duplicates as % of initial concentration.

i.e., the equilibrium position will be shifted along the isotherm curve to a lower equilibrium concentration. This is verified by the results shown in Table 17. It is interesting to note that, as shown in Table 17, the 'partition coefficient' ($\frac{x/m}{c}$) for adsorption remained essentially constant for both solution volumes.

5. The effect upon lindane adsorption of the cation on exchange complex and of H_2O_2-treatment of Venado clay

The adsorption of lindane from a benzene solution at 20°C on Ca- and Na-bentonite was measured. No significant difference in the concentration of the equilibrium solution was observed. Adsorption of lindane on Ca- and Mg-Venado clay from an aqueous solution (5.0 μg/ml) at 20°C was determined. In Table 18 these results are shown together with values for lindane adsorption on H_2O_2-treated Ca-Venado clay. Solution volume in this case was 20 ml. It is apparent from these data that changing the saturating cation from Ca^{++} to Mg^{++} has no apparent effect upon adsorption of lindane from aqueous solutions.

Table 18

Effect of Saturating Cation and H_2O_2-treatment upon Adsorption on Venado Clay from an Aqueous Solution (L.S. analysis)

Adsorbent	Equilibrium conc. (μg/ml)	Dev.	x/m (μg/gm)
Ca-Venado clay	0.373	0.2	18.5
Mg-Venado clay	0.372	0.1	18.5
Ca-Venado clay (H_2O_2-treated)	0.745	0.2	17.0

On the other hand, a definite reduction of the x/m value is effected by the H_2O_2-treatment of Venado clay. This is clearly indicated by the G.C. analysis as well as by the L.S. analysis. The reduction is undoubtedly due to the partial loss of organic matter. But, as shown in Table 8, even the H_2O_2-treated Venado clay contained 1.2% carbon, slightly more than one-third of the carbon content of the soil which had not been so treated. Now, we have noted that Venado clay soil contains approximately 40% montmorillonite. And the x/m value for the adsorption of lindane on Ca-bentonite (comprised essentially of montmorillonite) from a 5.0 μg/ml aqueous solution is of the order of 10 μg/gm, as shown in Table 20. Consequently, comparing 10 to 17 μg/gm, one must conclude that adsorption of lindane from aqueous solutions is influenced considerably by that portion of the organic matter which is quite resistant to the H_2O_2-treatment and which is probably, in effect, adsorbed strongly on the clay surface.

6. Effect of time period in water bath upon concentration of bulk solution

Elementary kinetic studies on the adsorption of lindane from benzene, nanograde hexane, and aqueous solutions were performed. When sampling was done before the 20-hour shaking period was up, the shaking was stopped five minutes before the sampling time, and then resumed as soon as sampling was completed. Table 19 summarizes the results of these time studies of adsorption on Ca-Venado clay.

Table 19

Solution Concentration as Affected by the Time Period in the Bath before Sampling

(Values given represent the concentration of lindane in µg/ml when the adsorbent was Ca-Venado clay, by L.S. analysis)

Time period between initial solution addition and final sampling (hours)	Initial Solution Concentration					
	50 µg/ml in benzene at 25°C		100 µg/ml in nanograde hexane at 20°C		1.0 and 5.0 µg/ml in water at 20°C	
	Final soln. conc.	Dev. (%)	Final soln. conc.	Dev. (%)	Final soln conc. from 1.0 µg/ml	Final soln conc. from 5.0 µg/ml
1/2	49.21	0.7				
5	48.62	0.3				
25	47.97	0.1				
70	48.74	0.7	33.5	0.9	0.0676	0.467
112					0.0630	0.445
120	48.57	0.5				
160					0.0609	0.437
240			39.6	3.1		

For the benzene solution it can be concluded that equilibrium is essentially established five hours after the addition of the solution to the adsorbent. The difference between the concentration values at 70 and 120 hours (48.74 and 48.57) is within experimental error. It is not clear why the concentration is lowest at the 25-hour sampling period. In the case of the hexane solution, the ambient concentration apparently increased from the 70-hour time to the 240-hour time. Considering the two aqueous solutions, the concentration in both cases declined steadily over the time period of 70 to 160 hours. However, with the 5.0 µg/ml initial solution, gas chromatographic analysis indicate some definite decomposition of lindane at 160 hours (about 0.020 µg/ml) with the possibility of some decomposition at 112 hours. (Such decomposition in concentration units represents the amount by which the concentration obtained by G.C. analysis is less than that obtained by L.S. analysis.) Comparison of G.C. data with L.S. data for the hexane solutions showed a decomposition of lindane of 20.0 µg/ml after 240 hours, but only 5.1 µg/ml after 70 hours. This increased level of decomposition at 240 hours may explain why the solution concentration as measured by liquid scintillation counting rose during the period from 70 to 240 hours. The decomposition products perhaps had a lower adsorptive affinity for the soil than did lindane. Gas chromatographic analysis of the benzene solutions indicated decomposition at 120 hours of the order of 3 µg/ml and no decomposition at 70 hours.

After consideration of the above facts, the writer decided that after a total of 70 hours from the addition of the solution to the time of sampling, adsorption equilibrium is essentially established for each solvent system. There was evidence, further, that decomposition of lindane began or increased if sampling was prolonged much more than 70 hours after the addition of the solution.

Adsorption of lindane on several adsorbents from four solvents

A summary of the experiments on adsorption of lindane from solutions of a single concentration at 20°C is given in Table 20. The values in the columns headed by 'D' represent the total amount of lindane (in µg.) in the 25-ml solution volume which had decomposed.

1. Discussion of adsorption affinities of lindane

Let us first direct our attention to only the x/m values shown in Table 20. The adsorption differences between solvents may be assumed to be due in part to the differing solubilities of lindane in them, and, in part, to the structure and affinity of the solvent molecule for the particular adsorbent. It is apparent, first of all, making allowance for the differences in initial concentration, that lindane most effectively competes for adsorption sites with water, and is least effective when competing with ethanol. To generalize for the adsorbents employed, we may say that the adsorption of lindane from the solvents increases in the following order: ethanol < benzene < hexane < water. With the exception of the position of ethanol, the other three solvents are arranged in the order of decreasing solubility of lindane. One can hypothesize, then, that the combination of ethanol's polarity plus its organophilic character is important in making it most effective in competing with lindane for adsorption sites.

Table 20

Adsorption of Lindane on Several Adsorbents at 20°C and the Degree of Accompanying Decomposition

Adsorbent	Solvent and Initial Concentration of Solution							
	Benzene 100 µg/ml, 10 grams of adsorbent, with exception of starred adsorbents		Nanograde hexane 100 µg/ml, 10 grams of adsorbent, with excep. of starred adsorbents		Ethanol 5 µg/ml, 5 grams of adsorbent		Distilled water 5 µg/ml, 5 grams of adsorbent	
	x/m (µg/gm)	D (µg)	x/m (µg/gm)	D (µg)	x/m (µg/gm)	D (µg)	x/m (µg/gm)	D (µg)
$Mg(OH)_2$*	6.4	2470	66.4	2170				
Alumina (basic)	2.7	2450	80.6	1690				
Alumina* (neutral)			68.6	2150				
Silica gel	13.5	145	245.0	0	-1.1	0	9.70	0
Ca-Oakley sand							9.40	0
Ca-Columbia Silt loam	2.8	234	94.1	0	+0.35	0	16.3	0
Ca-Venado clay	12.1	166	166.0	165	-0.30	1.8	22.5	0
Ca-bentonite	-2.2	96	97.2	0	-0.60	0	10.3	0
Na-bentonite*	-1.9	47	72.5	0				
Na-nontronite*	-2.3	0						
Ca-kaolinite					+0.15	2.3	2.70	0
Na-kaolinite*	-1.3	0	50.7	24				
Ca-Staten peaty muck	-1.2	169	38.8	0	3.70	0	24.6	0
Cation Exch. resin (H^+)*	-1.6	0	-1.8	224			24.6	0
Anion Exch. resin*	-1.6	70	+1.4	124			20.6	0

*Five grams of adsorbent employed in all cases.

The adsorption data of Table 20 for each solvent except ethanol are rearranged in the order of increasing adsorption in Tables 21, 22, and 23. With a few exceptions the order of adsorbents shown in Table 21 is the same as that in Table 22. Ca- and Na-bentonites show a negative affinity for lindane in benzene, while in hexane positive adsorption on these clays occur. The position of $Mg(OH)_2$ has been moved up in hexane, relative to benzene. Finally, the adsorption on Na-kaolinite is significantly greater than on Staten peaty muck in hexane, while in benzene there is no significant difference in adsorption between the two.

Table 21

Adsorption of Lindane from 100 µg/ml benzene solution

Adsorbent	x/m (µg/gm)
Na-nontronite*	-2.3
Ca-bentonite	-2.2
Na-bentonite*	-1.9
Cation Exch. Resin*	-1.6
Anion Exch. Resin*	-1.6
Na- kaolinite*	-1.3
Ca-Staten peaty muck	-1.2
Alumina (basic)	2.7
Ca-Columbia silt loam	2.8
$Mg(OH)_2$*	6.4
Ca-Venado clay	12.1
Silica gel	13.5

Table 22

Adsorption of Lindane from 100 µg/ml nanograde hexane solution

Adsorbent	x/m (µg/gm)
Cation Exch. Resin*	-1.8
Anion Exch. Resin*	1.4
Ca-Staten peaty muck	38.8
Na-kaolinite*	50.7
$Mg(OH)_2$*	66.4
Alumina (neutral)*	68.6
Na-bentonite*	72.5
Alumina (basic)	80.6
Ca-Columbia silt loam	94.1
Ca-bentonite	97.2
Ca-Venado clay	166.0
Silica gel	245.0

*Five grams of adsorbent employed.

Since the solubility of lindane in benzene is about 14 times that in nanograde hexane, it is understandable why lower x/m values were obtained for the benzene system. But, in addition, the competitive effectiveness of the benzene molecule may be greater than that of hexane, perhaps due to the differing molecular shape and electrical properties. The shape of the benzene molecule may have been important in adsorption on the Ca- and Na-kaolinites. Being a more 'compact' molecule than hexane, benzene could perhaps be more easily adsorbed in the spaces between the exchangeable Ca^{++} ions on the oxygen surfaces. And, the cross-sectional area of benzene corresponds closely with that for lindane. The benzene molecule is planar, while the γ-BHC molecule is not. Thus, lindane has little apparent advantage in terms of its size or shape over benzene, while it is more compact than the hexane molecule.

The low level of adsorption of lindane on Staten peaty muck from hexane or benzene indicates that these solvent molecules compete more effectively on such organic 'surfaces' than on crystalline surfaces. Apparently interaction of the lindane dipole with organic polar groups is not too important, yet lindane should be able to compete effectively for such sites against the non-polar hexane and benzene molecules on Staten peaty muck. The oxygen and hydroxyl surfaces of silica gel, clays, and alumina apparently have the greatest affinity for lindane in these two solvents. One can conclude, then, that the polarity of lindane may be important in the adsorption on such surfaces, and, thus, that the molecules may be oriented on the surface, probably with the positive side toward the surface. However, dispersion forces may also be effective here tending to make the adsorbed lindane molecules assume a co-planar orientation with respect to the surface. In the case of silica gel, there is little or no decomposition, and the surface is relatively unencumbered with attracted cations. This condition is apparently required for maximum adsorption of lindane in benzene or hexane.

A desorption experiment was conducted following the conclusion of an adsorption study in hexane. The hexane equilibrium solution was decanted off from each flask, and the adsorbents were dried under a hood in the flasks for one week. At the end of this period, 25 ml of reagent grade benzene was added to each flask. The flasks were stoppered and then shaken in the 20°C water bath for 12 hours. Then, after being at rest for 5 1/2 hours, the sampling was performed as described previously for benzene or hexane systems. Analysis was done both by L.S. counting and G.C. The results showed that in the case of silica gel and Venado clay almost the exact amount calculated to have been adsorbed was desorbed into the benzene. For the two bentonites, Ca-Staten peaty muck, and Ca-Columbia silt loam, the quantity of lindane apparently desorbed exceeded (by a factor as great as 2.5, for the Na-bentonite) the amount calculated to have been originally adsorbed from hexane. The amount desorbed from the basic alumina was somewhat less than the amount adsorbed and was entirely made up of decomposition products. No other decomposition products in the amounts desorbed were found except in the case of Ca-Venado clay in which case about 6% of the amount desorbed was determined to consist of decomposition products. It is felt that the reliability of this method for measuring the true amount of adsorbate desorbed is not good. The difficulty of volatilizing off all the lindane deposited on the surface of the adsorbent, during evaporation of the remaining portion of the hexane, is evidenced in the excess desorption values obtained for some of the adsorbents. At least one can tentatively conclude that adsorption of lindane on these adsorbents appears to be fully reversible when benzene is used as the desorbing solvent.

Referring again to Table 20, we see there is no definite adsorption of lindane from ethanol except on Ca-Staten peaty muck. This gives us another indication that the polar character of lindane is important in its adsorption on silica gel, clay minerals, and Venado clay. For it is apparently the strong polar nature of ethanol together with its tendency to form hydrogen bonds which allows it to compete so effectively against lindane on these adsorbents. The positive adsorption of lindane from ethanol on Staten peaty muck leads one to conclude that the non-polar organic constituents of this soil may have more affinity for lindane than for ethanol.

Table 23

Adsorption of Lindane from
5.0 μg/ml aqueous solution

Adsorbent	x/m (μg/gm)
Ca-kaolinite	2.70
Ca-Oakley sand	9.40
Silica gel	9.70
Ca-bentonite	10.3
Ca-Columbia silt loam	16.3
Anion Exch. resin	20.6
Ca-Venado clay	22.5
Cation Exch. resin	24.6
Ca-Staten peaty muck	24.6

Referring to Table 23, the order of adsorption from water has been changed considerably compared to the benzene or hexane systems. The exchange resins and the muck, as well as Venado clay, exhibit the highest affinity for lindane. It is apparent that water molecules would not be attracted to the non-polar organic constituents which make up the matrix of the exchange resins as well as a considerable part of the muck soil. So, with such solvent competition eliminated it is understandable why the highest x/m values were obtained for these materials. This also should explain why a significantly higher degree of adsorption occurred on Ca-Venado clay compared to Ca-bentonite. Unlike the latter, the former contained some organic material much of which is no doubt closely connected with the clay surface. The higher x/m values for Columbia silt loam compared to bentonite can be related to the former's organic matter content.

The fact that water as a dipole can offer some competition for adsorption sites on crystal surfaces of clays, silica gel, and sand, accounts for the lower adsorption values for lindane on these adsorbents relative to the organic-type (or organic matter-containing) adsorbents. Had it not been for the low solubility of lindane in water and its consequent high chemical potential in aqueous solution, less adsorption on these adsorbents could be expected in competition with water. Because, although the dipole moment of water is less than that for lindane (1.84D compared to 2.84D for lindane), water tends to form hydrogen bonds with such surfaces. And it is likely that the type of hydrogen bond formed by water (O-H------O) with oxygen surfaces is of greater energy than that possibly formed by lindane (C-H------O). This is because of the greater polarity of the O-H group compared to C-H. (The C-H bond moment has been estimated as 0.4D and that for O-H has been calculated as 1.52D.[5])

The lower x/m value for Ca-kaolinite compared to that for Ca-bentonite (in table 23) may likely be due to the lower specific surface area of the former. Assuming a specific surface for kaolinite of 15 m^2/gm, and utilizing the total specific area determined for Ca-bentonite (810 m^2/gm.), one can compute the amounts adsorbed per unit surface area. These values are found to be 0.18 μg/m^2 for Ca-kaolinite and 0.0127 μg/m^2 for Ca-bentonite. On this basis, assuming that interlayer adsorption of lindane on bentonite does occur, it would appear that lindane can compete with water much more effectively on the hydroxyl surfaces of kaolinite than on the oxygen surfaces of bentonite. If this is true, one would expect, by observing the closeness of the x/m values for silica gel and bentonite in Table 23, that the degree of hydroxylation of the silica gel surface is low. (The silica gel employed and bentonite have surface areas of the same order of magnitude.) It is interesting to observe that the x/m values for Ca-Oakley sand and silica gel correspond closely. One might hypothesize from this that the particular crystalline structure of silica is not of great importance with respect to lindane adsorption from water.

With regard to the adsorption of lindane from water on silica surfaces, the writer earlier performed an experiment which measured the adsorption of completely untagged lindane from water on sodium glass beads (200μ and 29μ sizes) at 24°C. The glass beads were washed several times with distilled water and air-dried. Nineteen grams of the beads were weighed into each 250-ml Erlenmeyer flask. One hundred milliliters of a saturated aqueous solution of lindane (7.30 μg/ml), or a half-saturated aqueous solution (3.65 μg/ml), were added to each flask in duplicate. The flasks were shaken for 33 hours and sampling was carried out one hour after the shaking was stopped. Extractions were carried out into benzene, and the analysis was performed by electron-capture gas chromatography. The results are shown in Table 24.

Table 24

Adsorption of Lindane from Aqueous Solutions
on Na-glass beads at 24°C

Initial Concentration (μg/ml)	x/m (μg/gm) Average bead diameter 29μ	 200μ
3.65	16.0	6.0
7.30	31.8	13.5

The values for the adsorption on 200-micron beads correspond well with the value of 9.7 μg/gm (Table 23) obtained for the adsorption of lindane on silica gel from a solution of initial concentration of 5.0 μg/ml. Both the x/m value and the initial solution concentration in the latter case are about midway between the respective two values for the 200-micron beads. The particle size of silica gel used (100-200 mesh) is in the same range as the 200-micron beads. The higher adsorption values for the smaller diameter beads must be related to the greater specific surface area of the latter. But the increase of adsorption is proportionately lower than the increase of surface area. The ratios of x/m values for 29μ beads compared to the 200μ beads is 2.35 and 2.65 for the saturated and half-saturated initial solutions, respectively. While the ratio of specific surface areas of 29μ beads compared to 200μ beads is 6.90.

Although in previous paragraphs of this section the importance of the dipole character of lindane in its adsorption on crystal surfaces has been suggested, the importance of dispersion forces cannot at all be dismissed. Considering equation (1), which is the expression for the energy of adsorption due to dispersion forces, we see that differences in the energy of adsorption between solute and solvent must lie in the factor, λ. This factor, λ, is equal to 3/4 $\alpha_1\alpha_2 \cdot 1/2(I_1 + I_2)$, where α_1 is the algebraic mean polarizability of the clay ions, α_2 the polarizability of the adsorbed molecule, I_1 the mean ionization potential of the clay ions, and I_2 the ionization potential of the adsorbed particle. It was not possible to obtain a value for the ionization potential of lindane. Thus, it is impossible to calculate even an estimate of the ratio of λ for lindane to that for any of the solvents employed. Nevertheless, the polarizability (α) for lindane and for each solvent at room temperature has been calculated by use of the equation[5]

$$\alpha = \frac{3M}{4\pi N\rho}\left[\frac{n_R^2 - 1}{n_R^2 + 2}\right] \qquad (54)$$

where M is the molecular weight, ρ the density, N Avogadro's number, and n_R the index of refraction. The value of n_R for γ-BHC was obtained from reference no. 1. The n_R values for the solvents were obtained from the Handbook of Chemistry and Physics, 42nd edition. The results of the calculation are given in Table 25.

Considering the affect of polarizability alone one might predict adsorption of lindane on a crystalline surface from the solvents to increase in the following order: hexane < benzene < ethanol < water. But, referring to Table 20, we see that the true order of adsorption with respect to the organic solvents is reversed. On the basis of polarizability alone one would expect definite positive adsorption on crystal surfaces from all four solvents. In any case, because of the lack of data on ionization potentials, we are unable to evaluate the relative contribution of dispersion forces to the adsorption of lindane in the systems studied. The data lead us to conclude that dipole-dipole forces are important in the adsorption of lindane on crystalline surfaces from the solvents employed. The contribution of dispersion forces may be important, but is unclear.

Table 25

Polarizability of Lindane and Solvents

Compound	n_R	T (°C)	$\alpha \times 10^{24}$
γ-BHC	1.636	25	21.9
Benzene	1.501	20	10.4
n-hexane	1.375	20	11.8
Ethanol	1.360	20	5.10
Water	1.333	20	1.47

2. Decomposition of lindane in initial studies

As is evident from Table 20, definite decomposition of lindane occurred in hexane and benzene solutions in contact with several adsorbents. It may be helpful to arrange some of this data in the order of increasing pH of the adsorbents as measured in distilled water (Table 26).

There seems to be a definite relationship between the acidity of an adsorbent in distilled water and the extent of decomposition of

Table 26

Decomposition of Lindane in Benzene and Hexane at 20°C

Adsorbent	pH (measured in distilled water)	Amount of Lindane decomposed (in μg)	
		In benzene solution**	In hexane solution**
Silica gel	4.4	145	0
Ca-Staten peaty muck	6.6	169	0
Ca-Columbia silt loam	7.5	234	0
Ca-bentonite	8.3	96	0
Ca-Venado clay	8.5	166	165
Alumina (neutral)*	8.15	-	2150
Alumina (basic)	10.0	2450	1690

*Only 5.0 grams of adsorbent used in experiment.
**Initial solution concentration 100 μg/ml.

lindane in benzene and hexane. The only exceptions to this trend in benzene systems are Ca-bentonite and Ca-Venado clay. It might be postulated that the clay surface in some way acts to reduce the degree of decomposition. Cases have been noted in the literature, however, in which clay actually acted to catalyze a decomposition reaction.[89] It may be that in the case of benzene solutions hydroxyl groups are not readily ionized at the clay surface, so that the effective pH level at the surface is reduced. While in the same solvent at the alumina surface hydroxyl groups may be readily ionized and released.

In the case of hexane solutions no decomposition of lindane occurred except with adsorbents having a definitely alkaline reaction. The difference between the amounts decomposed with 'neutral' and basic alumina may simply be due to the difference in the mass of the two adsorbents employed. More decomposed products could be adsorbed on the 10.0 grams of basic alumina. The difference between the amount decomposed with Ca-Venado clay and with 'neutral' alumina obviously cannot be related to the pH of the adsorbents in distilled water. As observed for benzene solutions, the clay surface in hexane solutions must release hydroxyl groups much less readily than the alumina surface. This same effect may explain the low level of decomposition of lindane on Venado clay measured in ethanol solutions.

Brief attention will be paid to the nature of the decomposition products in hexane and benzene systems containing $Mg(OH)_2$, neutral alumina, and Ca-Venado clay. Figures 7, 8, and 9 represent the gas chromatograms on which are shown the peaks of lindane and of the major decomposition products. Chromatograms of the $Mg(OH)_2$- and alumina-containing systems (figures 7 and 8) represent injections of undiluted solutions. More complete decomposition seems to be indicated with $Mg(OH)_2$ in hexane solutions than in benzene solutions. In the case of the $Mg(OH)_2$ -benzene system a small amount of lindane remains, and, in addition, a large peak appeared (the second peak after the solvent peak), representing a probable intermediate product. This could well represent a pentachlorocyclohexene. For the $Mg(OH)_2$-hexane system no such intermediate product nor lindane appeared in the chromatogram. But with both solvents a large peak appeared containing three fused peaks (the first peak immediately after the solvent peak).

FIGURE 7

GAS CHROMATOGRAM
(CCLUMN-5% S.E. 30)
γ-BHC - $Mg(OH)_2$ SYSTEMS
EQUIL. SOLUTION (NO DILUTION)

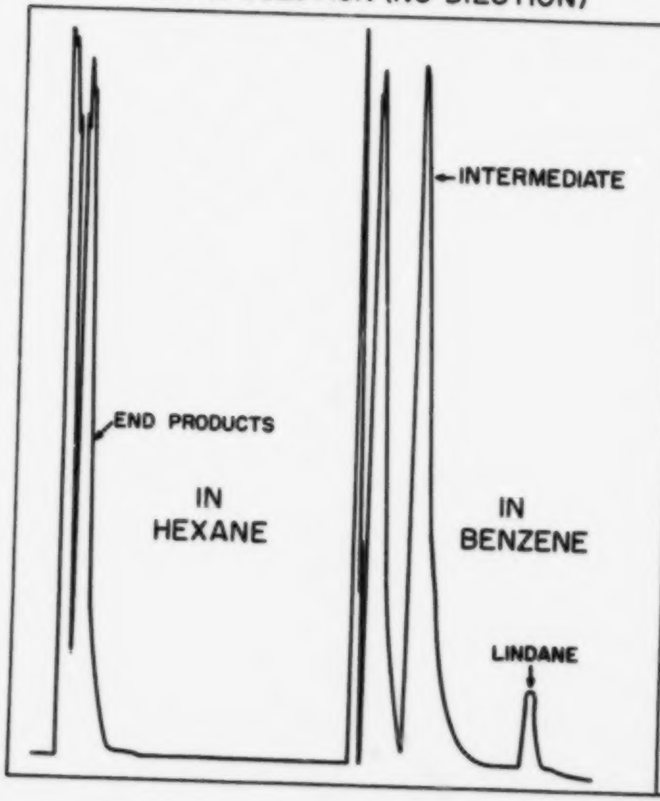


FIGURE 8

GAS CHROMATOGRAM
(COLUMN-5% S.E. 30)
γ-BHC-NEUTRAL ALUMINA-
HEXANE SYSTEM
EQUIL. SOLUTION (NO DILUTION)

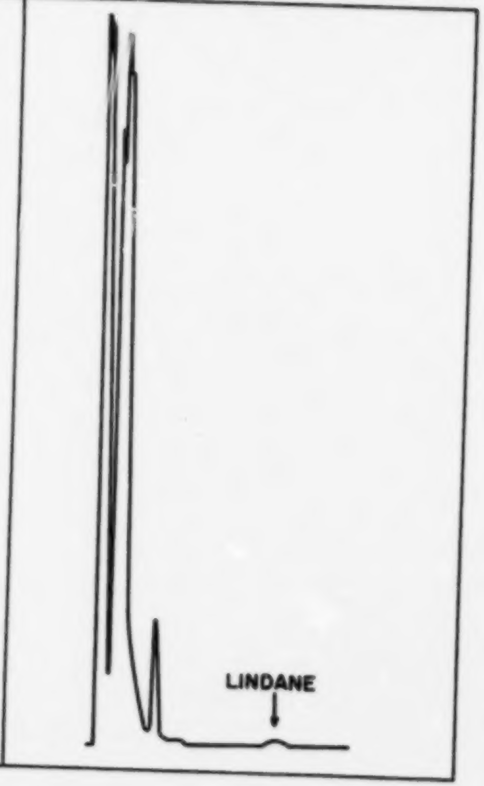
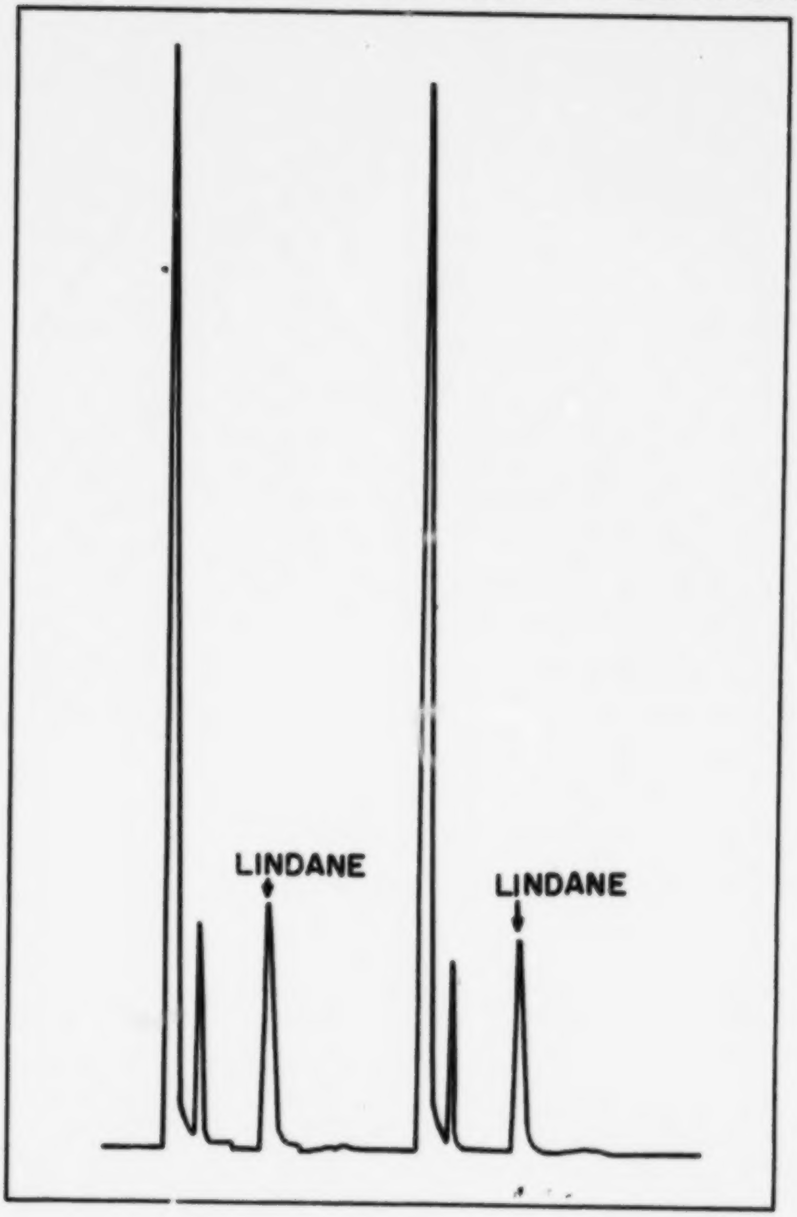


FIGURE 9

GAS CHROMATOGRAM
(COLUMN-5% DOW 11)
γ-BHC-Ca-VENADO CLAY-
HEXANE SYSTEM
INITIAL SOLN. CONC. -100μg/ml
1000:1 DILUTION OF EQUIL. SOLUTION



It is believed that this composite peak represents the three trichlorobenzenes which are the end products of the drhydrochlorination of lindane. For the 'neutral' alumina-hexane system in addition to the large initial peak, possibly representing trichlorobenzenes, a small peak appeared representing the possible intermediate product and a very small lindane peak.

The chromatogram for the Ca-Venado clay-hexane system (figure 9) represents a 1000:1 dilution of the equilibrium solution. The column used in this case was different from that used in obtaining chromatograms of solutions in the $Mg(OH)_2$ and alumina systems. But by comparing retention times relative to lindane, it is apparent that the additional peak appearing in the Venado clay system is identical to that tentatively identified as a pentachlorocyclohexene in the $Mg(OH)_2$ case. In the chromatogram of the equilibrium solution for the Venado clay-benzene system (not shown) an extremely small peak representing the intermediate product appeared, in addition to the lindane peak.

As shown in Table 20, no decomposition of lindane was indicated for any of the adsorbents used in aqueous systems. The lower initial concentration of the aqueous solutions may partly explain why decomposition was not apparent there, but occurred in the higher concentration benzene and hexane solutions.

In many cases where zero decomposition is recorded for the aqueous and ethanol systems, the equilibrium concentration of the bulk solution determined by gas chromatography was found to be actually greater (by as much as 20%) than that determined by liquid scintillation counting. This was also found true in the hexane solutions containing Ca-bentonite, Ca-Staten peaty muck, and Ca-Columbia silt loam. It is difficult to explain this phenomenon in cases when differences clearly exist between the results of the two analyses. One troublesome possibility is that in some way the C^{14}-labeled molecules behave differently from the unlabeled molecules.

Such 'isotope effects' have been discussed by Aronoff[2] and by Chase.[12] The 'isotope effect' is evidenced by a difference in reaction rates and/or equilibrium positions between tagged and untagged molecules. Isotope effects are generally thought to be due to the difference between the masses of the radioisotope and the normal isotope. The heavier the element, the lower the relative magnitude of such an isotope effect. The ratio of the mass of C^{14} to that of C^{12} is 1.17. It is conceivable that such mass differences could result in somewhat different adsorptive behavior between tagged and untagged BHC molecules. In the case of these experiments in which small amounts of the C^{14}-tagged BHC isomer were combined with the untagged BHC isomer, such a possible difference in adsorptive behavior would result in the tagged molecules not being strictly representative of all the BHC molecules in the system. But it is clear that the tagged molecules acted in a manner reasonably representative of the untagged molecules; for liquid scintillation analysis of solutions in the isotherm studies show an expectable increase in the net counts per minute with increasing initial concentration. As noted before, the tracer concentration was constant in all solutions. If the labeled molecules behaved completely differently from the unlabeled ones, at the low surface coverage involved one would expect essentially the same final net cpm for every solution. It was mentioned previously that the accuracy and precision of quantitative gas chromatographic analysis is less than half that of liquid scintillation counting. This may help to explain the excess concentration values obtained by gas chromatography. But if the inaccuracy of the gas chromatographic method is the cause, the values obtained for decomposition cannot be considered very reliable either. It seems reasonable that the isotope effect could be partially responsible for the G.C. concentration values being in excess of the L.S. values. The data indicate, nevertheless, that the radioactive tracer used was generally closely representative of the entire BHC species present, labeled and unlabeled.

Decomposition of lindane in aqueous solutions at room temperature was demonstrated in an experiment in which varying amounts of meta-sodium silicate were added to a saturated aqueous solution of lindane containing no adsorbent. To ten milliliters of a saturated aqueous solution of lindane in a glass-stoppered test tube was added the proper amount of reagent grade $Na_2SiO_3 \cdot 9H_2O$. The experiment was carried out in triplicate. The test tubes were shaken and placed in the dark for 70 hours. After this period each sample was extracted into nanograde hexane and the analysis performed by gas chromatography. The results are shown in Table 27, together with the pH of the resulting solutions. A peak representing the intermediate product appeared at the lowest concentration of $Na_2SiO_3 \cdot 9H_2O$ and increased in size with increasing concentration of the silicate. But at the highest concentration this peak didn't appear at all. The retention time of the intermediate product was 0.33 relative to lindane. This is identical to that of the peak shown in figures 7 and 9 which is believed to represent a pentachlorocyclohexene. At a pH level of 10.4 the lindane concentration had been reduced to a little more than one-third of its initial

FIGURE 10

DECOMPOSITION OF LINDANE IN AQUEOUS SOLUTIONS OF META SODIUM SILICATE

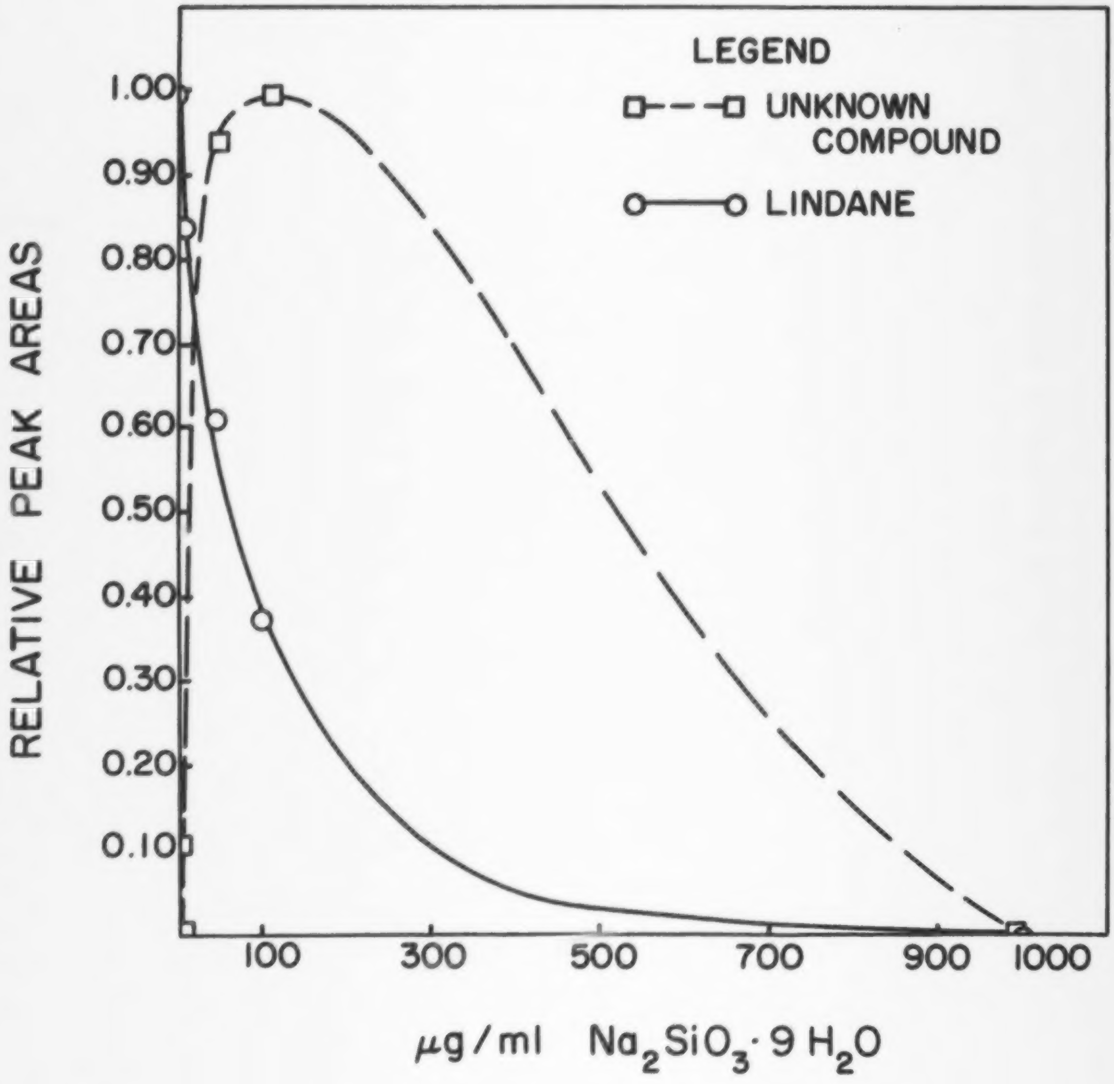


Table 27

Decomposition of Lindane in Aqueous Solutions of Meta Sodium Silicate

Conc. of $Na_2SiO_3 \cdot 9H_2O$ (μg/ml)	Average Relative Peak Areas Lindane	Intermediate product	pH
0	1.00	0.00	6.3
10	0.84	0.10	8.7
50	0.61	0.94	9.7
100	0.37	1.00	10.4
1000	0.0002	0.0000	11.4

concentration, and the concentration of the intermediate was at a maximum. At a pH of 11.4 essentially all the lindane and the intermediate had been decomposed, but a peak very near the solvent peak, most probably representing trichlorobenzenes, appeared. The values given in Table 27 are plotted graphically in figure 10. We may conclude that decomposition of lindane in water is closely related to the pH of the solution. Loss of more than 15% of the lindane in aqueous solution due to decomposition can be expected only when the pH level rises above 9.0.

Isotherm studies of γ-BHC and β-BHC

The choice of the adsorbents and solvents to employ for the isotherm studies was made after consideration of the data of the initial adsorption studies. Adsorption levels were considered to be too low from benzene and ethanol solutions to permit accurate determination of isotherms over a range of low concentrations. The four adsorbents were chosen because they represent particular types of adsorbing surfaces common in soils, and because they exhibited considerable affinity for lindane in hexane and aqueous solutions. These adsorbents, Ca-Staten peaty muck, Ca-Venado clay, Ca-bentonite, and silica gel, represent, respectively, a high organic soil with a mixed mineral fraction, a clay soil high in montmorillonite, a montmorillonitic clay, and a crystalline silica. In addition to being representative of particular soils or soil fractions, these adsorbents showed relatively little or no tendency to catalyze decomposition of lindane in hexane or water.

Isotherms were obtained for the adsorption of γ-BHC and β-BHC from aqueous solutions at 20° and 30°C on all four adsorbents. Further, isotherms for the adsorption of γ-BHC from aqueous solutions at 10°C and 40°C on Ca-Staten peaty muck and Ca-Venado clay were obtained. Adsorption isotherms of γ-BHC from nanograde hexane solutions on these two adsorbents were obtained for different temperatures (10°C and 20°C for Ca-Staten peaty muck, and 10°, 20°, and 30°C for Ca-Venado clay). Because of the limited solubility of the two isomers in water the concentration range for these isotherms was restricted to very low concentrations. The concentration range was 0.056 to 5.0 μg/ml for the initial aqueous γ-BHC solutions, and 0.075 to 0.65 μg/ml for the initial aqueous β-BHC solutions. A considerably wider concentration range was adopted for the hexane solution isotherms -- 0.10 to 500.0 μg/ml.

In the β-BHC studies there was observed a definite discrepancy between the final concentration of the standard blank solutions (at the two highest concentrations) and the concentration of the corresponding standard solutions kept in storage. That is, there was a reduction in the concentration of the two highest standard solutions, apparently as a result of factors operating over the three-day period in the bath and during the centrifugation process prior to sampling. These concentration losses of the standard solutions are shown in Table 28. No additional peaks indicating decomposition products were observed in the chromatograms of these standard blank solutions. It is conceivable that the losses for the two highest concentration levels were due to volatilization occurring perhaps during the centrifugation-sampling procedure. Whatever the cause of the loss, the concentration of the equilibrium solutions and x/m values were calculated, as usual, on the basis of the final, not initial, concentrations of the standard blank solutions.

Table 28

Loss of Concentration of Standard Blank Aqueous Solutions of β-BHC over the Course of an Adsorption Experiment

(Values given are averages of several gas chromatographic determinations)

Initial conc. (μg/ml)	Final conc. (μg/ml)
0.075	0.074
0.18	0.191
0.38	0.361
0.53	0.424
0.65	0.460

Little or no isomerization was observed to have occurred during the isotherm studies either in the standard blank solutions or in the experimental flasks. No isomerization was observed for γ-BHC in either solvent. The possibility of slight isomerization of β-BHC occurring in the standard blank aqueous solutions was indicated by a very small peak (representing possibly the δ-isomer) following the peak for β-BHC. But the relative area of this additional peak was only 1/20th or less of that of the β-BHC peak.

Before presenting the results of the isotherm studies it would be appropriate to compare briefly the results of the two analytical methods employed. In Table A-2 in the Appendix are compiled the values for the equilibrium concentrations of the bulk solutions as determined by both methods of analysis. As was discussed in the previous subsection, the accuracy and precision of quantitative gas chromatography (G.C.) is considered to be definitely less than that for liquid scintillation counting (L.S.). The writer has concluded that deviations of the G.C. values from L.S. concentration values should exceed 8-10 percent before one can proceed to draw definite conclusions as to the occurrence of possible decomposition or other phenomena. In cases in which the possibility of decomposition was suspected (L.S. values exceeding G.C. concentration values), following this rule of thumb, unequivocal decomposition occurred in only one adsorbent-solvent system (Venado clay-hexane). All the G.C. values in this case were lower than the L.S. values by more than 10% at all three temperatures. In addition, definite peaks representing decomposition products of lindane appeared on these chromatograms, while for no other system did such peaks occur. The additional peak observed for the Venado clay-hexane system at 10° and 20°C was that representing the possible intermediate product, discussed earlier. At 30°C, in addition, two smaller peaks in the region close to the solvent peak also appeared. These perhaps can be identified with the peaks found with the $Mg(OH)_2$-hexane system and believed by the writer to represent trichlorobenzenes.

The only other systems where one can reasonably suspect decomposition to have occurred (on the basis of the 8-10% rule of thumb) are the β-BHC aqueous systems. Consideration of the values for the highest concentration level of β-BHC with Staten peaty muck and Venado clay indicate some decomposition. Yet, at 30°C the G.C. and L.S. values are essentially identical for Venado clay. This would throw doubt on the relative lowness of the G.C. values at the lower temperature. Only in the case of the β-BHC-silica gel-water system do the data consistently seem to indicate a degree of decomposition. Yet, no extraneous peaks occurred in the chromatogram of the equilibrium solution of this system. So, there is still room for reasonable doubt as to whether or not decomposition actually occurred in the β-BHC-silica gel system.

Significantly higher G.C. concentration values, relative to L.S. values, were the rule for the γ-BHC aqueous systems containing Staten peaty muck or Venado clay. This problem was discussed in the previous sub-section.

With the exception of the Venado clay-hexane system all isotherms were obtained from calculation based upon liquid scintillation analysis alone. Gas chromatographic results were treated as auxiliary data serving to indicate gross decomposition of the BHC isomers. The isotherms for the Venado clay-hexane system do not mean a great deal because of the existence of breakdown products in the system. Nevertheless, isotherms for this system were drawn so as to provide a rough comparison with the Staten peaty muck-hexane system. For the γ-BHC-Venado clay-hexane isotherms x/m values were computed as usual from the L.S. data, while c values were taken from the G.C. data, the latter values indicating the bulk concentration of undecomposed lindane alone.

1. Nature of isotherms obtained

The normal isotherms (x/m plotted against c) are presented in figures 11a, 12a, 13a, 14a, 15a, 16, and 17a. The data from which the isotherms were obtained are given in Table A-1 of the Appendix. The corresponding isotherms in which x/m values are plotted against the reduced concentration, c/c_o,(hereafter designated as the 'corrected' isotherms), are shown in figures 11b, 12b, 13b, 14b, 15b, and 17b. In each case, c_o represents the solubility of the isomer in the particular solvent at the given temperature, as determined by the writer. These data are presented in Table A-3 of the Appendix.

It is apparent from figures 11 and 12 that the isotherms for γ-BHC in water on all four adsorbents are nearly linear. The normal isotherms (figures 11a and 12a) show that an increase in temperature uniformly results in a lowering of adsorption for each of the systems. Proportionally, the decrease of adsorption with increased temperature is greatest with silica gel and least for Ca-bentonite. Figures 11b and 12b indicate the reverse situation. These corrected isotherms indicate an increase in adsorption with increase in temperature. One would, thus, expect the associated differential heats of adsorption to be positive. Only in the case of silica gel is there no apparent increase

FIGURE 11a

ADSORPTION OF γ-BHC FROM WATER

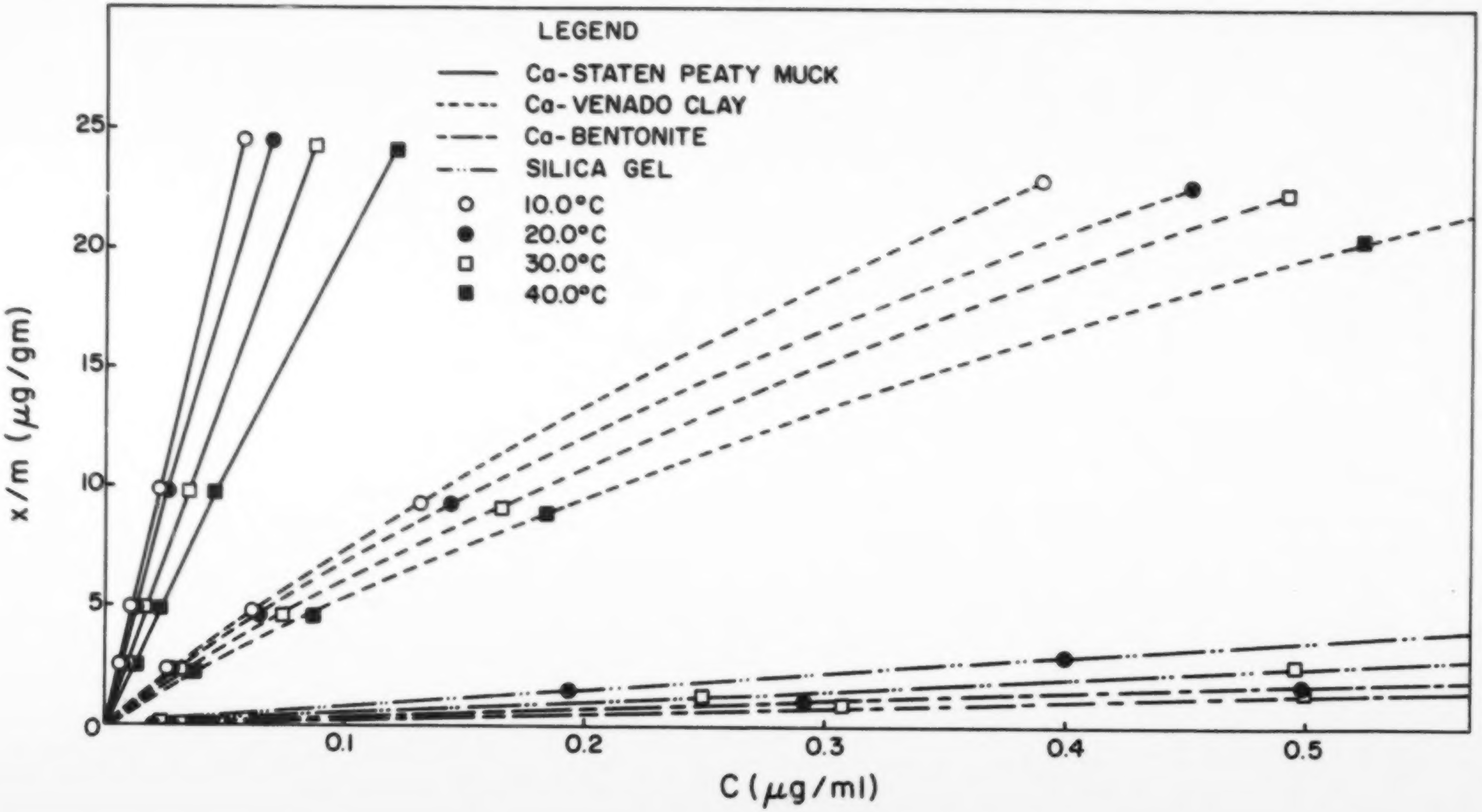


FIGURE 11b

ADSORPTION OF γ-BHC FROM WATER

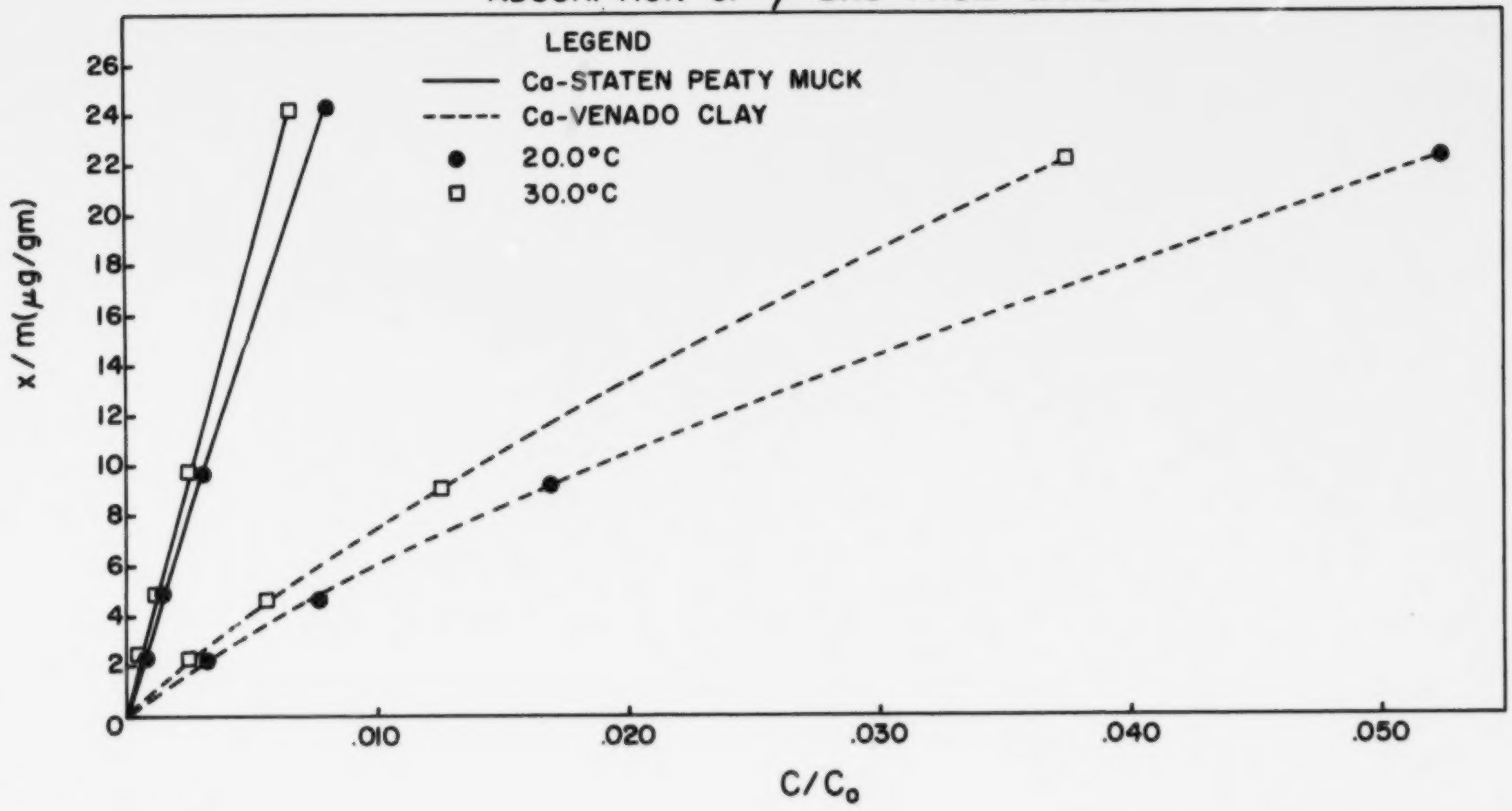


FIGURE 12a

ADSORPTION OF γ-BHC FROM WATER

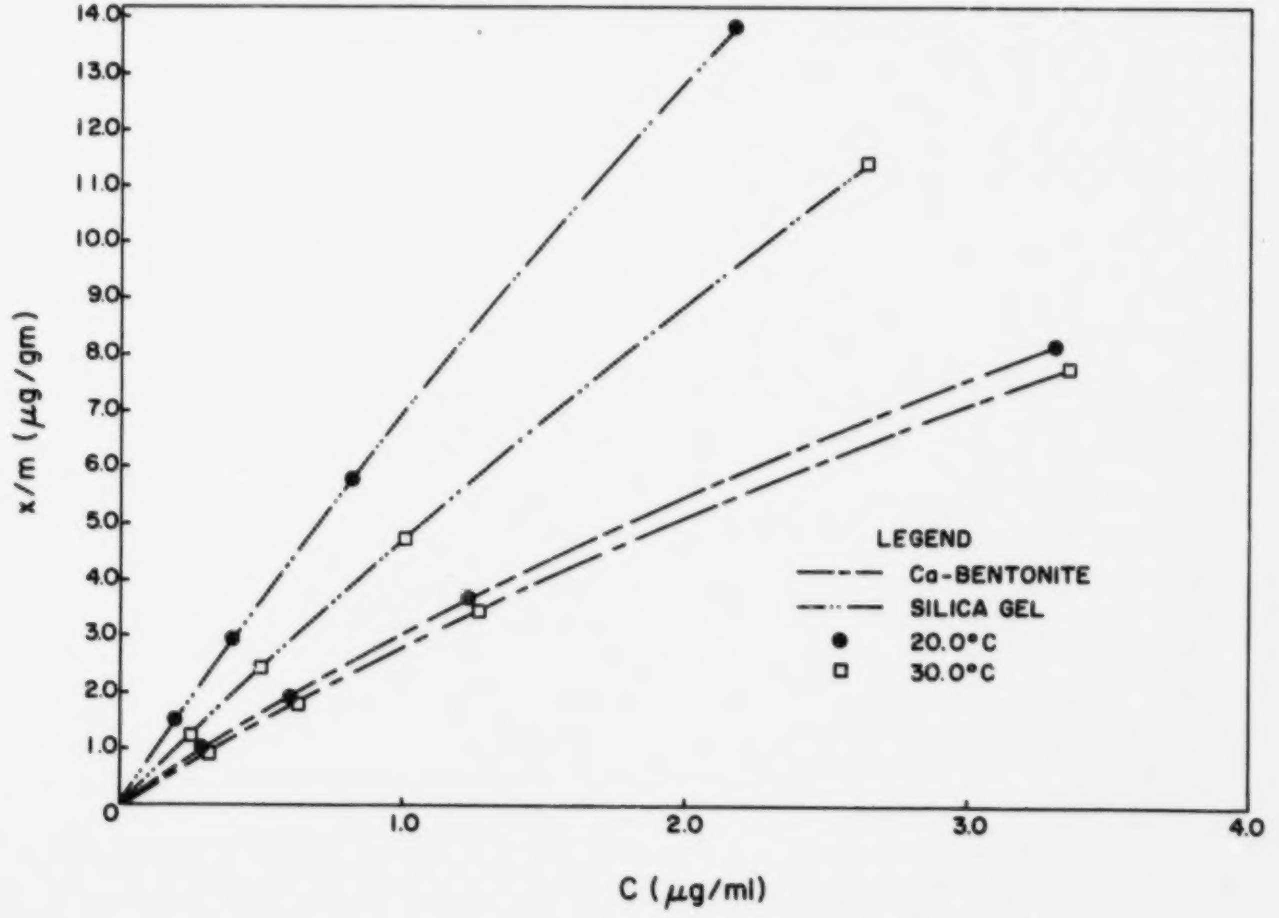
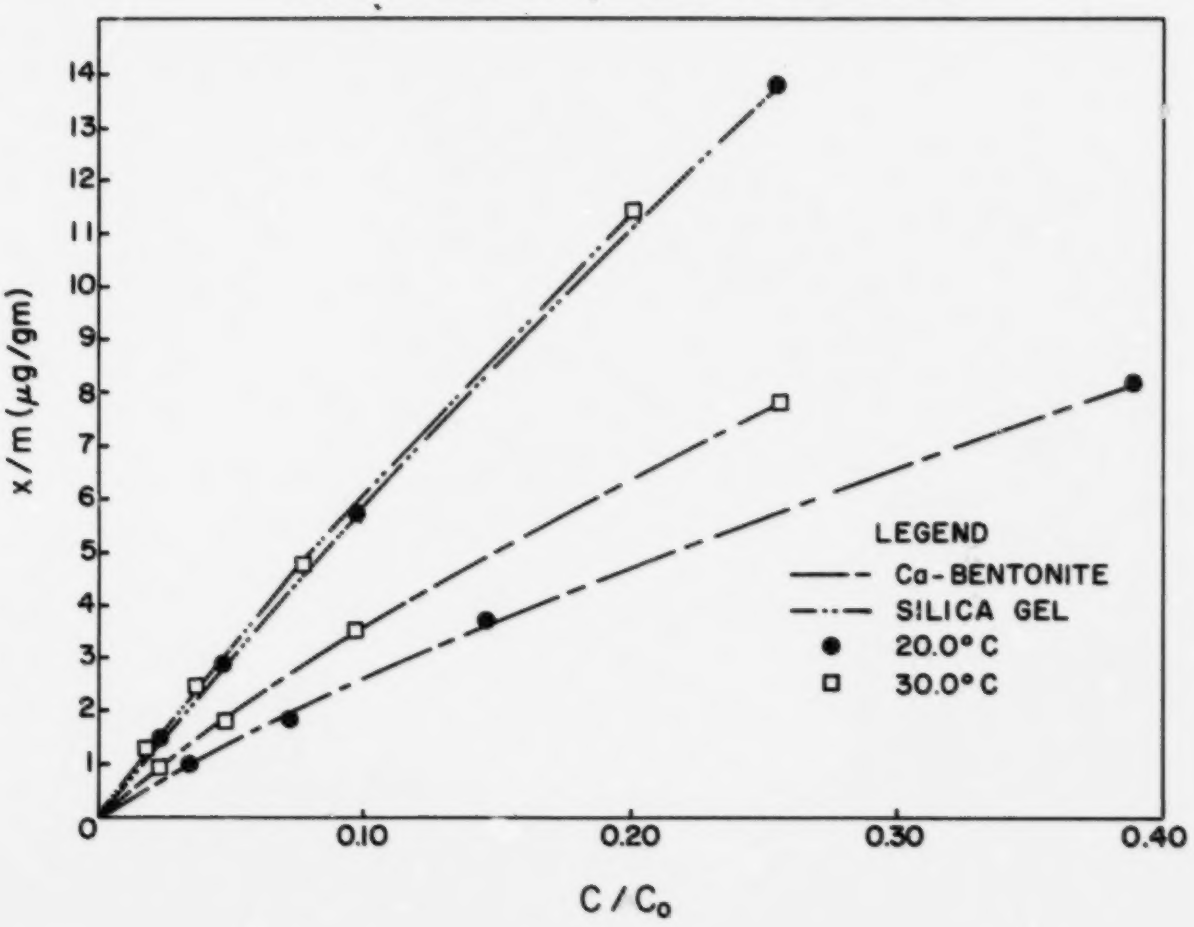


FIGURE 12b

ADSORPTION OF γ-BHC FROM WATER



in adsorption with increased temperature. Figure 12b indicates that adsorption in this case may proceed with essentially no heat effect, except for that involved in the solubility relationship. It would appear, then, that in these cases it is only the solubility-temperature effect which serves to make the adsorption process exothermic, while it would otherwise tend to be endothermic. The higher relative positions of the isotherms for Ca-Staten peaty muck and Ca-Venado clay, as seen in figure 11a, underscore the importance of organic matter in the adsorption of lindane from water.

The adsorption of β-BHC from aqueous solutions is seen in figure 13a to parallel closely the adsorption of aqueous γ-BHC on Staten peaty muck and Venado clay. The respective slopes of the curves in figures 11a and 13a correspond very well. If the highest concentration points are neglected these β-BHC isotherms also approach a linear form. The corrected isotherms of figure 13b show that, as for the aqueous γ-BHC systems, when the solubility-temperature effect is eliminated, adsorption is no longer exothermic. Although in the case of the corrected isotherm for β-BHC on Venado clay increased temperature resulted in increased adsorption, no apparent difference due to temperature is observed in the level of adsorption on Staten peaty muck, unlike the aqueous γ-BHC-Staten peaty muck system.

In figure 14a the normal isotherms for Ca-bentonite show that β-BHC adsorption increased slightly with temperature. This increase broadened considerably when the solubility effect was removed, as shown in figure 14b. A further difference relative to the aqueous γ-BHC systems is in the relative positions of the Ca-bentonite and silica gel isotherms. While silica gel exhibited a greater adsorption affinity for aqueous

FIGURE 13a

ADSORPTION OF β-BHC FROM WATER

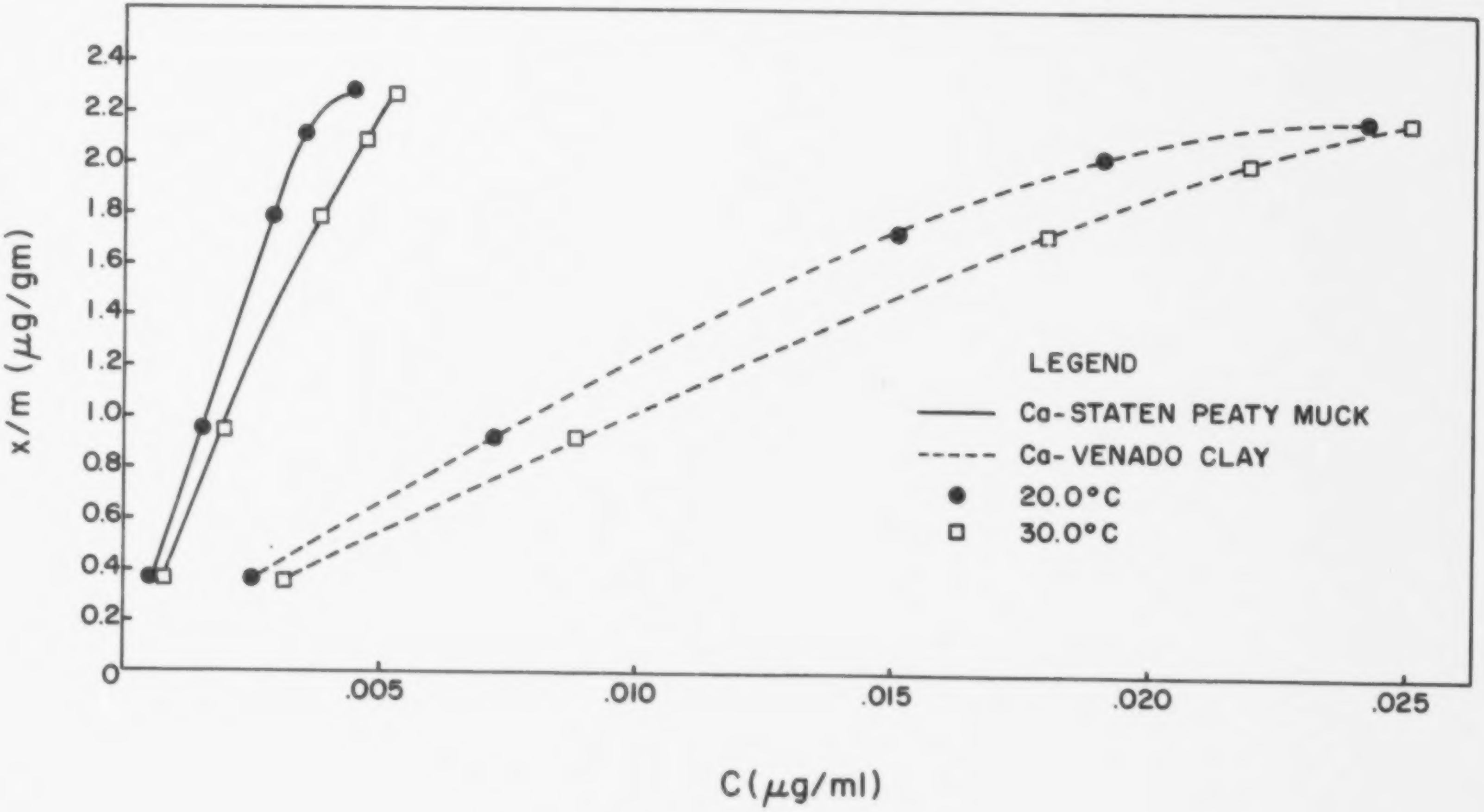


FIGURE 13b

ADSORPTION OF β-BHC FROM WATER

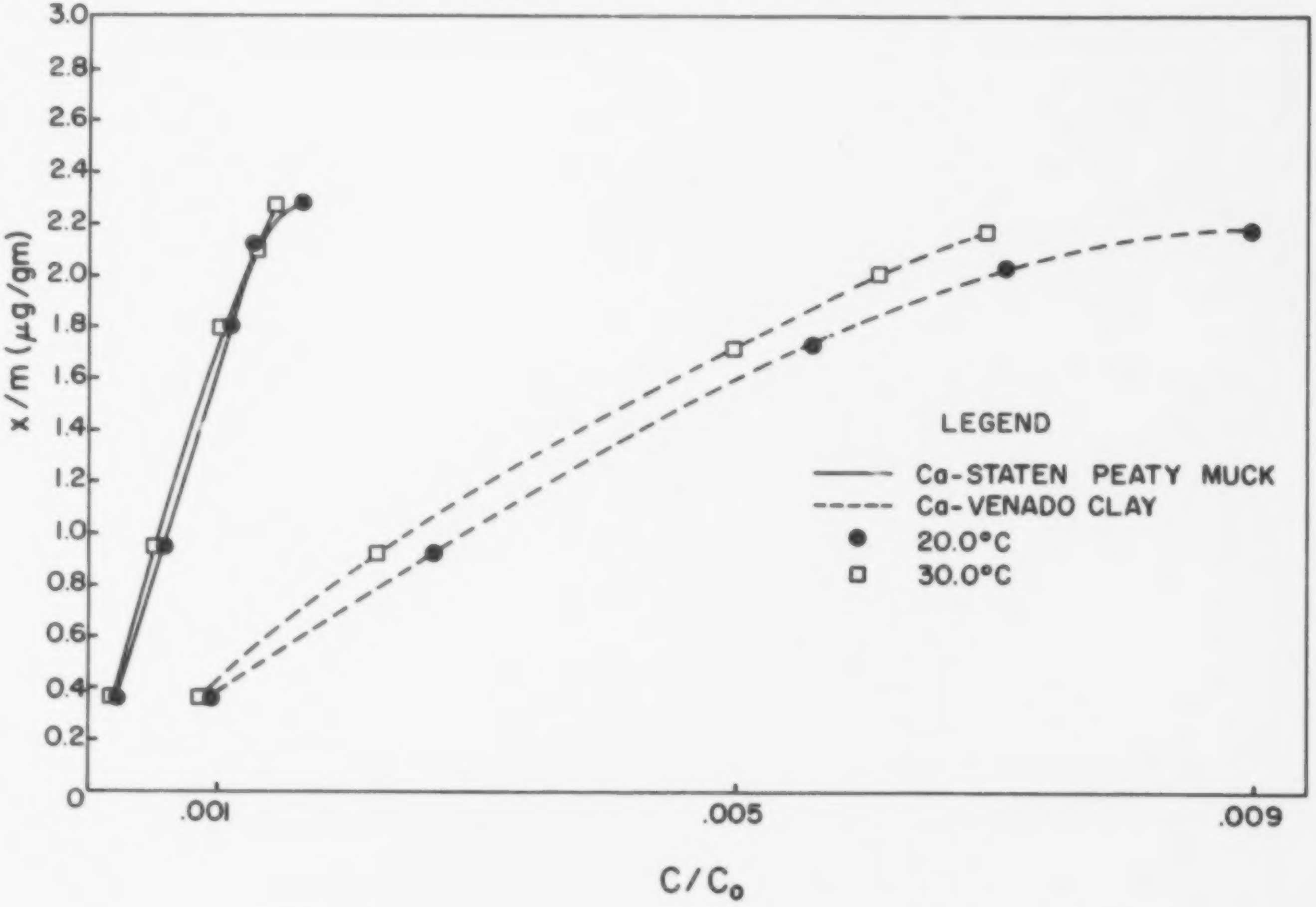


FIGURE 14a

ADSORPTION OF β-BHC FROM WATER

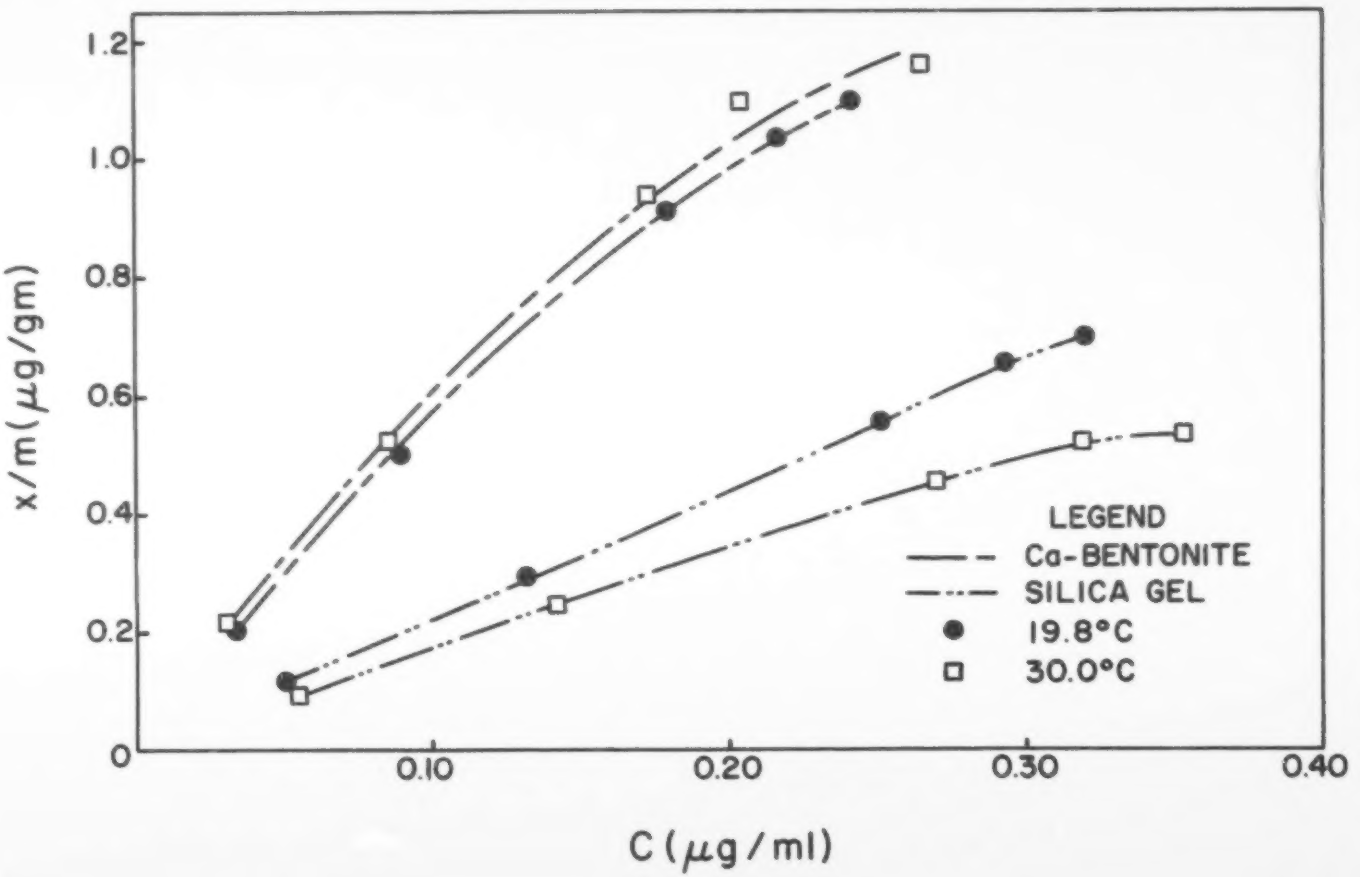
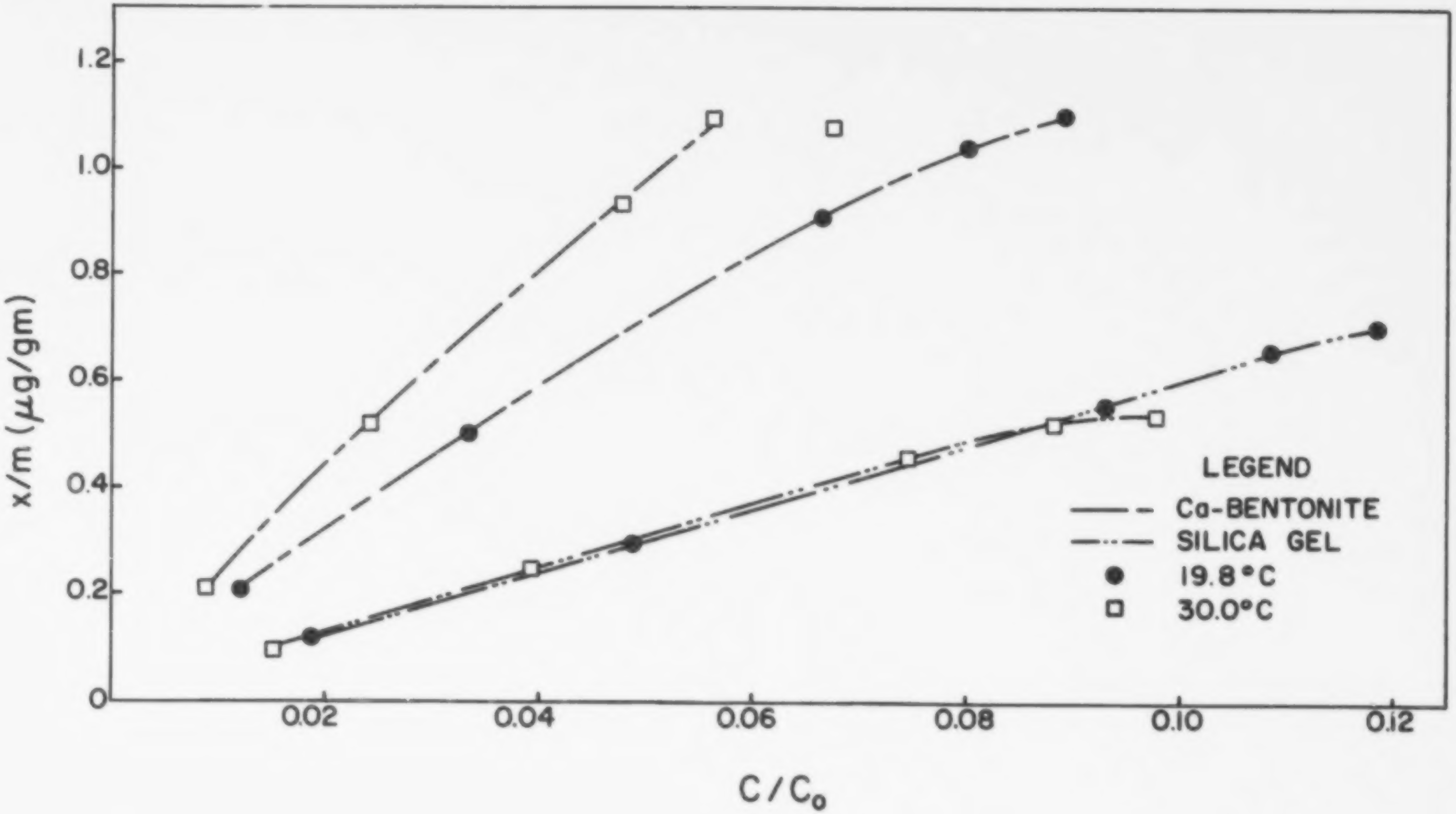


FIGURE 14b

ADSORPTION OF β-BHC FROM WATER



γ-BHC than did Ca-bentonite, the reverse is true for the adsorption of β-BHC. Similar to the aqueous γ-BHC case, the corrected isotherms for β-BHC on silica gel exhibit little or no temperature effect, i.e., heat effects other than those associated with solution are almost negligible.

The isotherms of γ-BHC adsorption from hexane are shown in figures 15, 16, and 17. The lesser degree of adsorption on Ca-Staten peaty muck compared to Ca-Venado clay is apparent throughout the concentration range. The isotherms for Ca-Staten peaty muck approach linearity particularly over the lower part of the concentration range. (See figure 17a in which only the five lowest concentration points are plotted.) It is clear from the normal isotherms in figures 15a and 16 that there is no consistent effect of temperature in the adsorption on Staten peaty muck over the whole range of concentrations studied. It is possible that at a certain surface coverage or concentration range the overall adsorption process changes from an exothermic to an endothermic one, as indicated in figure 16. But inspection of the corrected isotherms in figure 15b reveals that adsorption increases uniformly with temperature over the entire range. Over the lower part of the concentration range (figures 17a and 17b) both the normal and corrected isotherms reveal a uniform temperature effect and one that corresponds exactly with the temperature behavior of aqueous γ-BHC on the same adsorbent.

In figure 18 the loss of concentration of the bulk solution due to γ-BHC decomposition in the Venado clay-hexane system is plotted against the equilibrium concentration of γ-BHC for the three temperatures. The increase of decomposition apparent with the rise of temperature indicates that the decomposition reaction is endothermic.

FIGURE 15a

ADSORPTION OF γ-BHC FROM NANOGRADE HEXANE

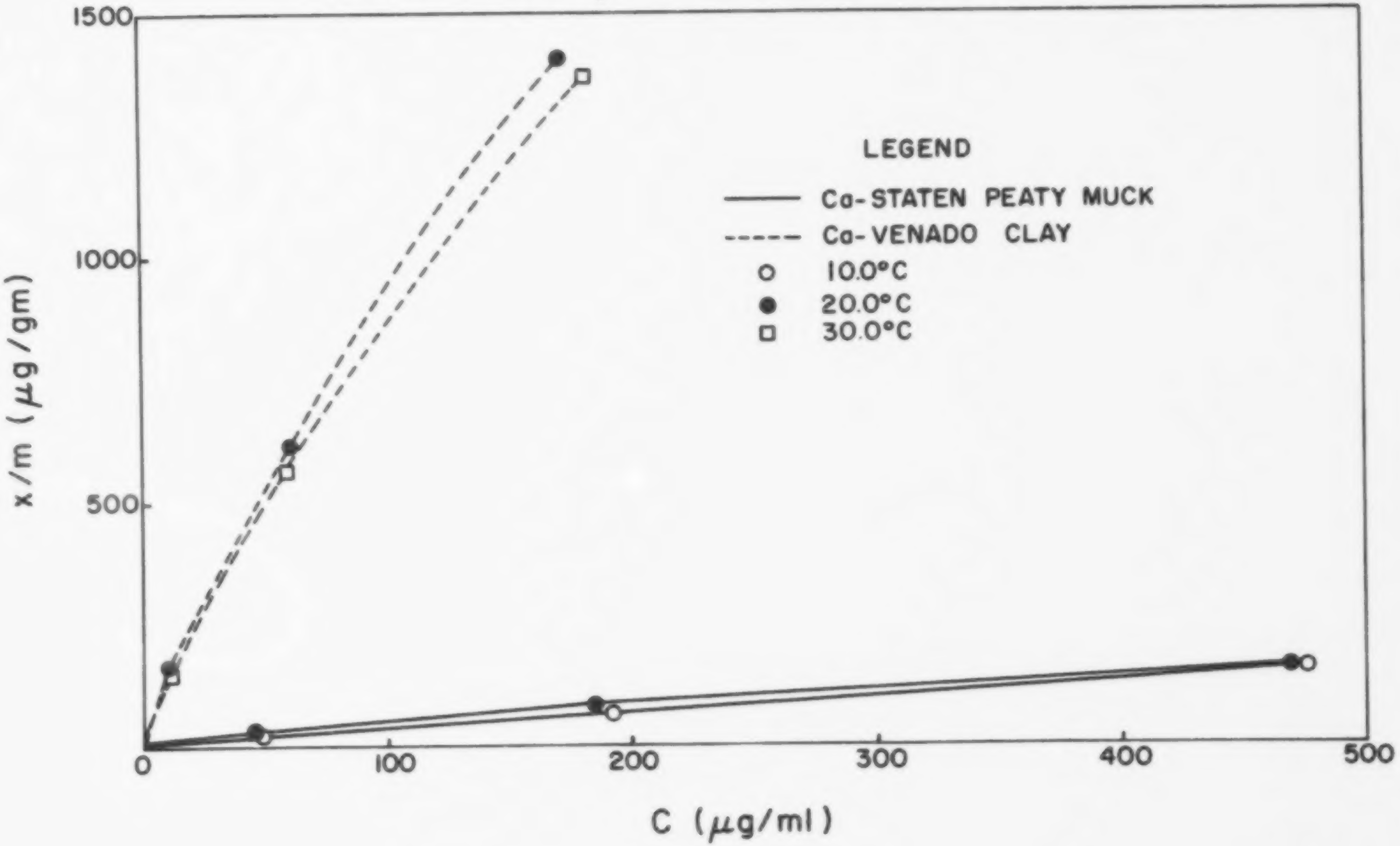


FIGURE 15b

ADSORPTION OF γ-BHC (IN NANOGRADE HEXANE) ON Ca-STATEN PEATY MUCK

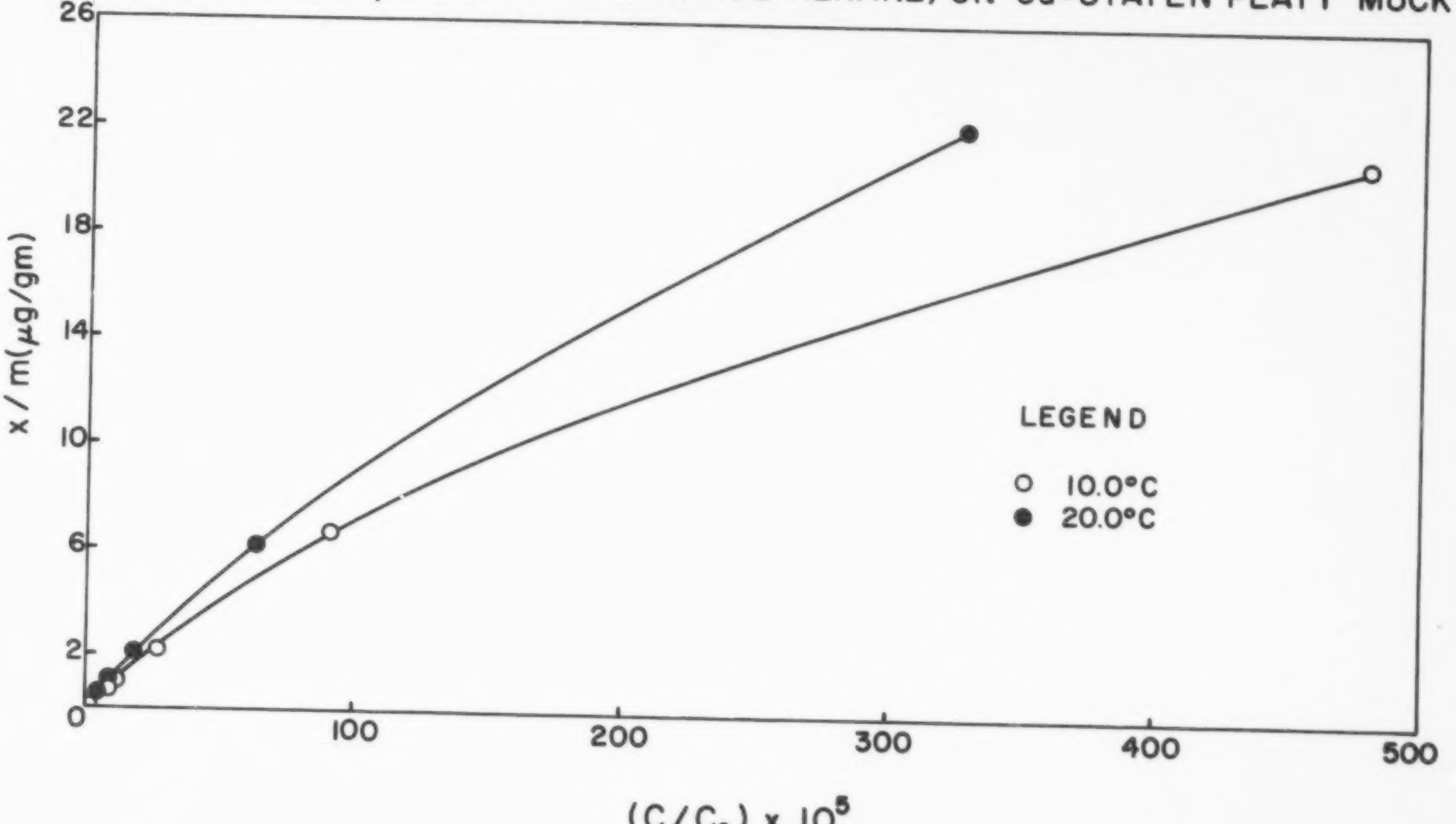


FIGURE 16

ADSORPTION OF γ-BHC FROM NANOGRADE HEXANE

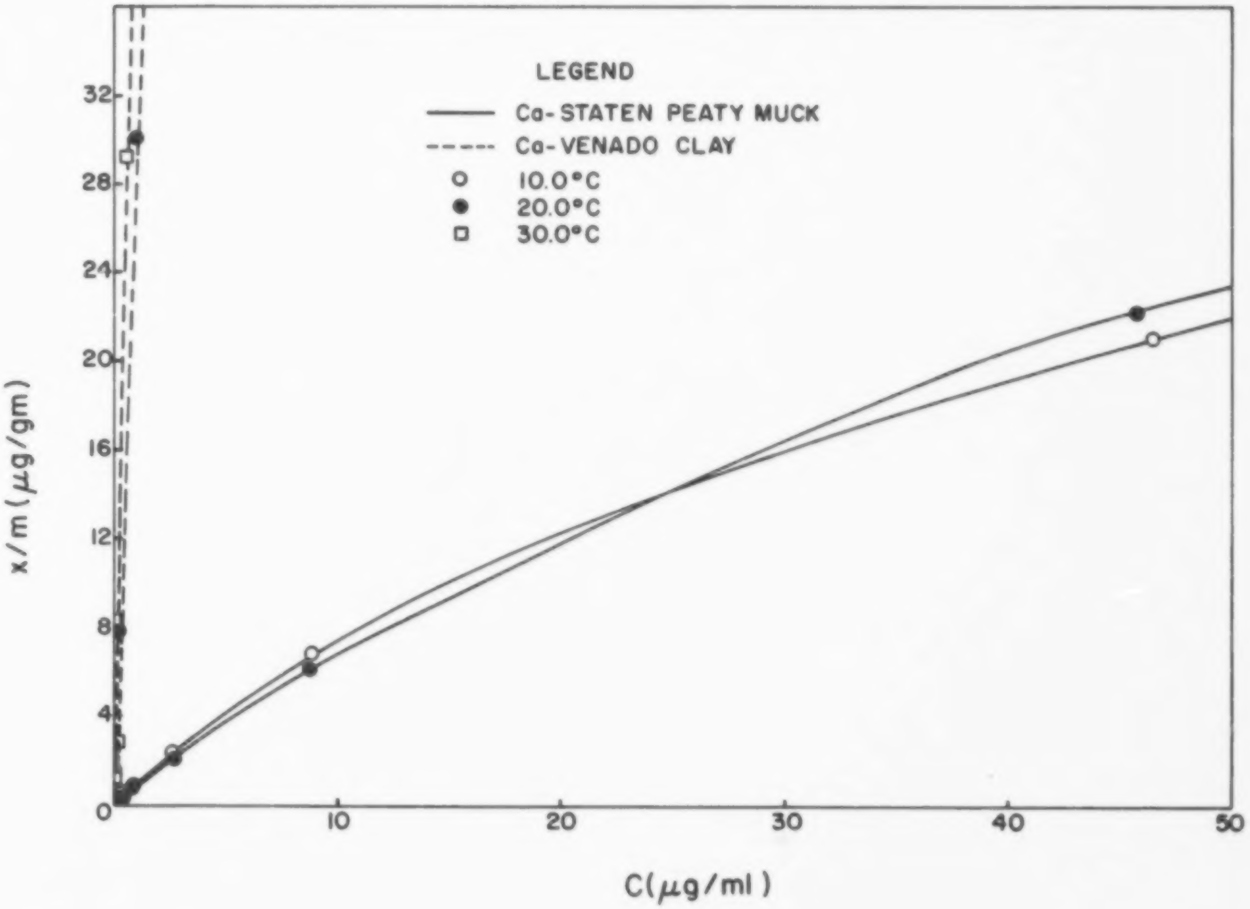


FIGURE 17a

ADSORPTION OF γ-BHC FROM NANOGRADE HEXANE
LOWEST 5 POINTS

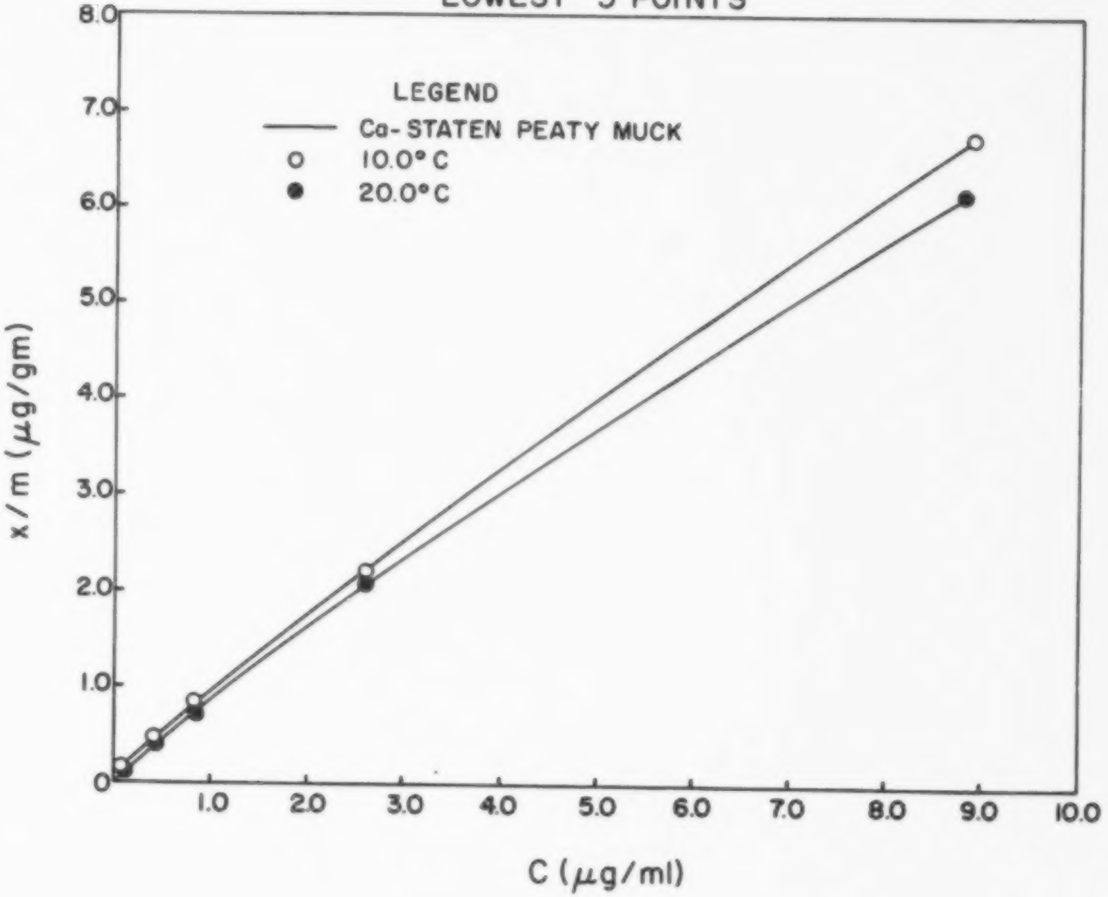


FIGURE 17b

ADSORPTION OF γ-BHC FROM NANOGRADE HEXANE

LOWEST 5 POINTS

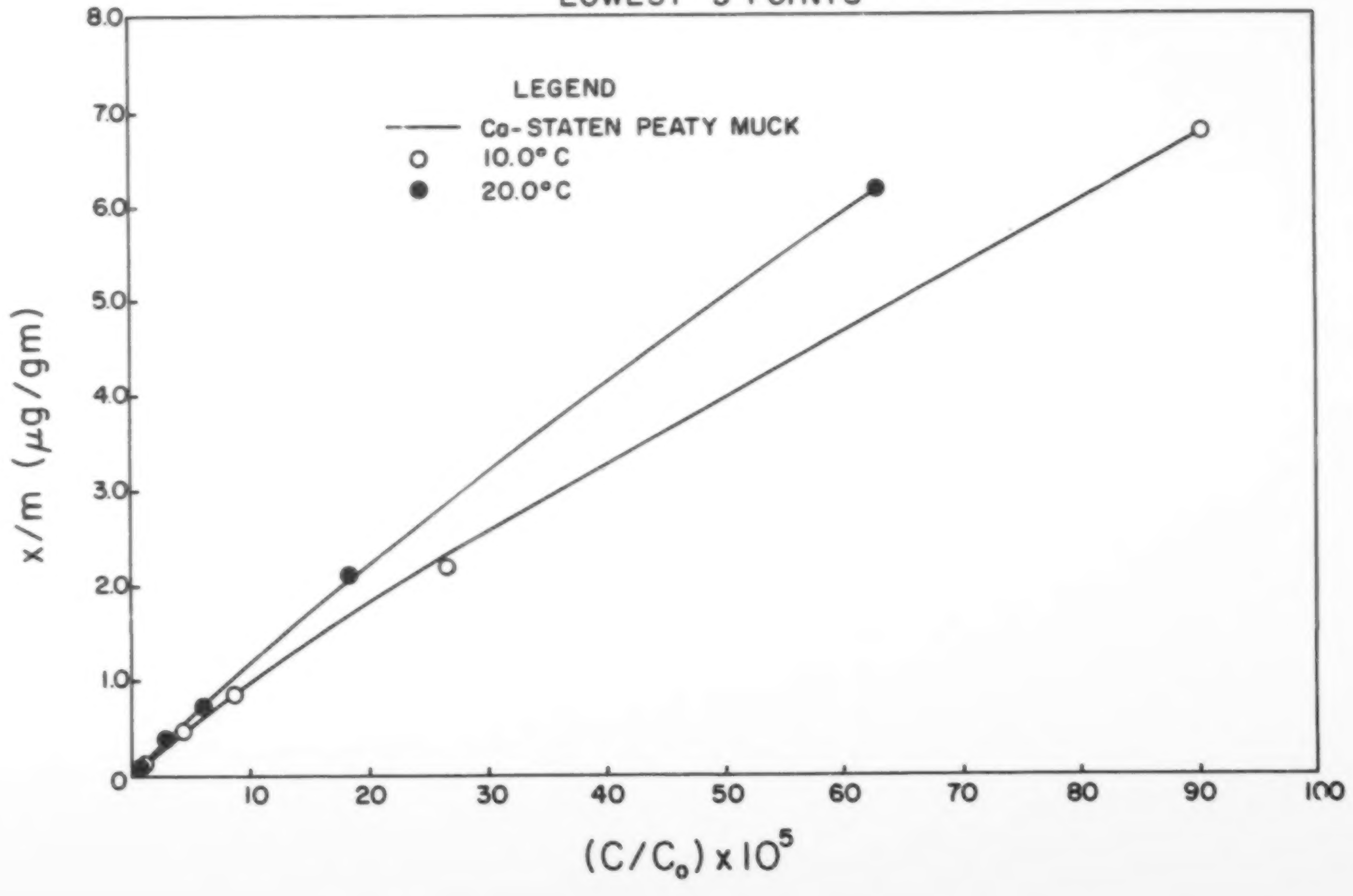
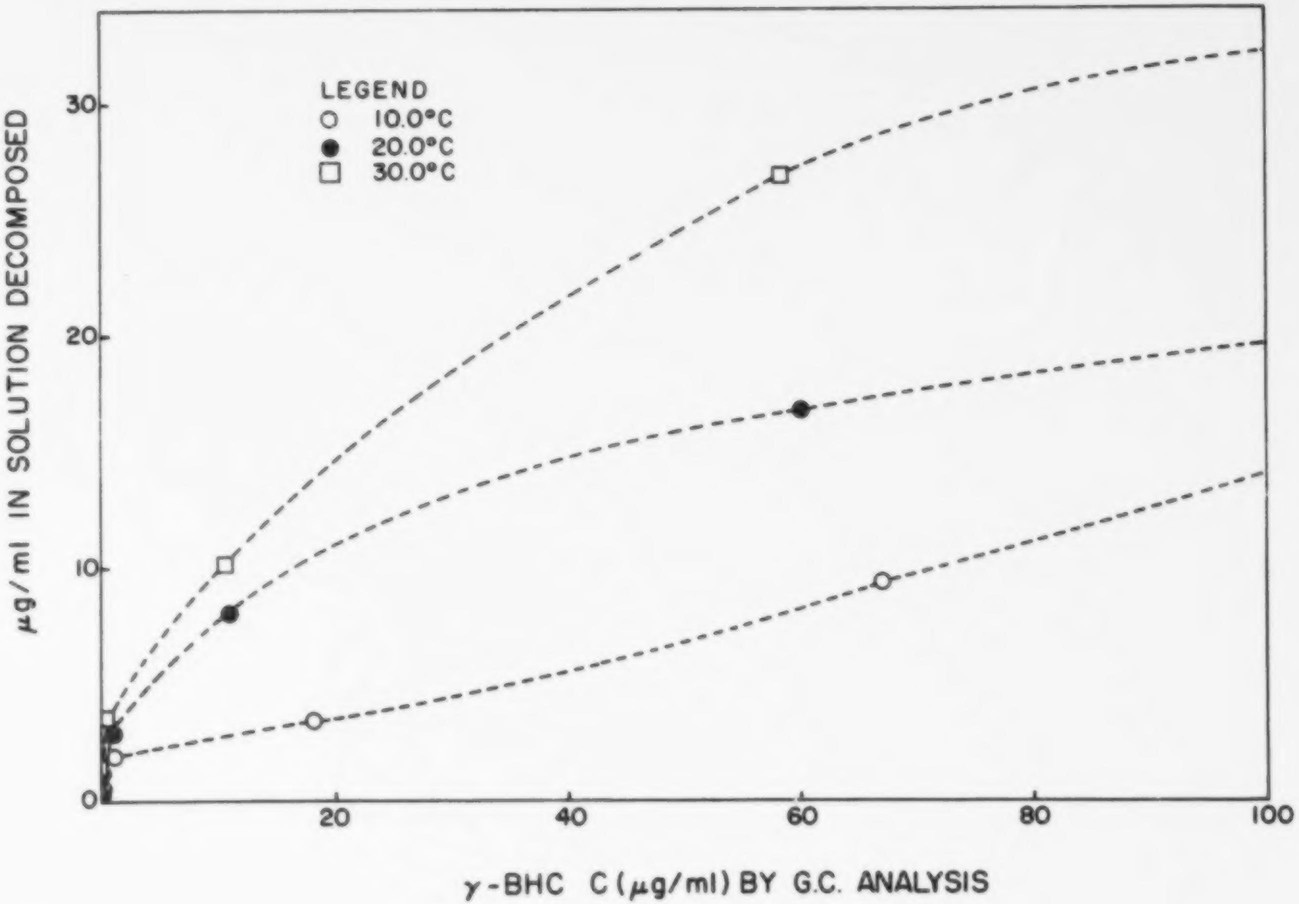


FIGURE 18

DECOMPOSITION OF γ-BHC ON Ca-VENADO CLAY IN NANOGRADE HEXANE



Graphs of $\frac{c}{x/m}$ versus c, according to the Langmuir equation (equation 13), in no case yielded linear plots. (See figures A-1, A-2, and A-3 in the Appendix.) Plots of log x/m vs. log c for all the γ-BHC aqueous isotherms yielded linear plots (figure 19). Nearly linear log-log plots were obtained for the lower concentration range of the Staten peaty muck-hexane isotherms (figure 20). The log-log plots for the β-BHC isotherms (figure 21) are essentially linear if the highest concentration point for each isotherm is ignored. Freundlich constants for the aqueous γ-BHC and β-BHC isotherms and for the γ-BHC-Staten peaty muck isotherms were determined by the least squares method. For the β-BHC isotherms, the highest concentration point was neglected in the calculation of these constants. Only the lowest five points were used to calculate the Freundlich constants in the case of the Staten peaty muck-hexane system. These constants are presented in Table 29. The constants k and k' refer to the intercept of the log-log plot when x/m is plotted against c and c/c_o, respectively. In each case k' was determined from the calculated k and 1/n values by means of the equality $k' = kc_o^{1/n}$, which follows from equation (19) if c/c_o is substituted for c. The same slope, 1/n, for the log-log plots holds regardless whether log c or log c/c_o is plotted on the abscissa.

With the exception of the β-BHC-bentonite-water system, the k values understandably decrease as temperature increases for each system. Similarly, the solubility-corrected intercept values, k', increase in each case as temperature increases. That all these isotherms are nearly linear in the arithmetic plots is indicated by the fact that the 1/n values all fall in a range close to one (0.86 - 0.99). (Fully linear arithmetic plots would of course yield 1/n values of unity.)

FIGURE 19
ADSORPTION OF γ-BHC FROM WATER (LOG-LOG PLOT)

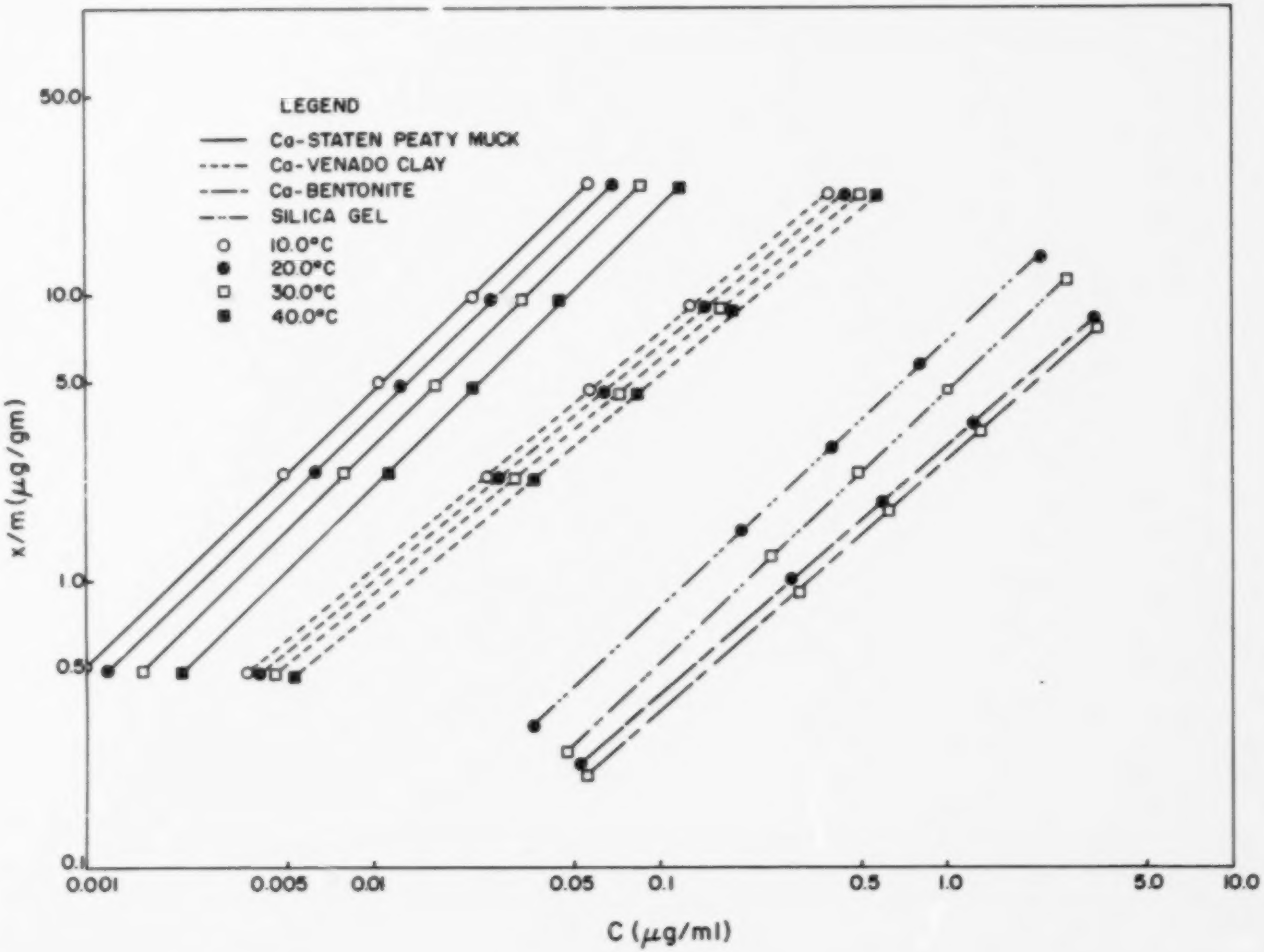


FIGURE 20

ADSORPTION OF γ-BHC FROM NANOGRADE HEXANE (LOG-LOG PLOT)
LOWEST 5 POINTS

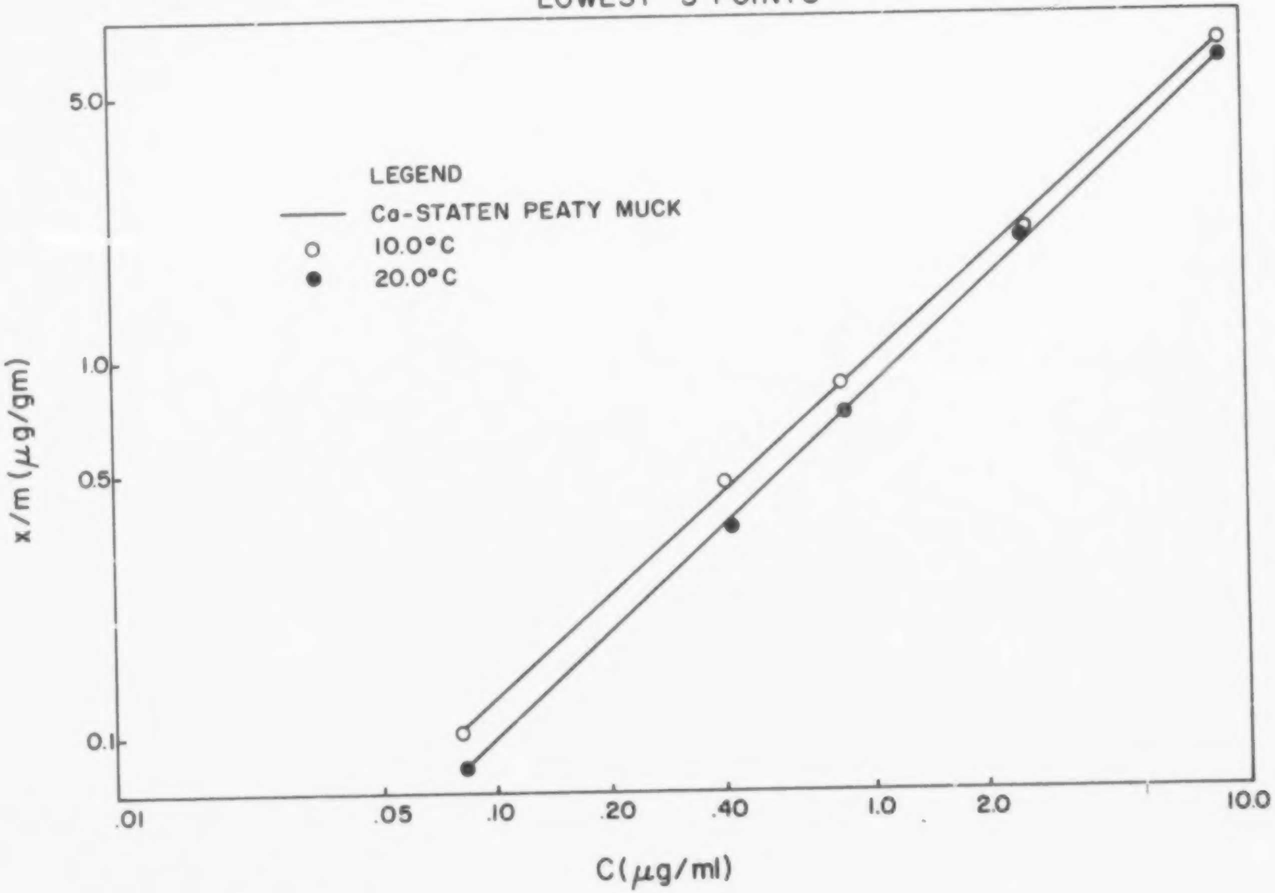
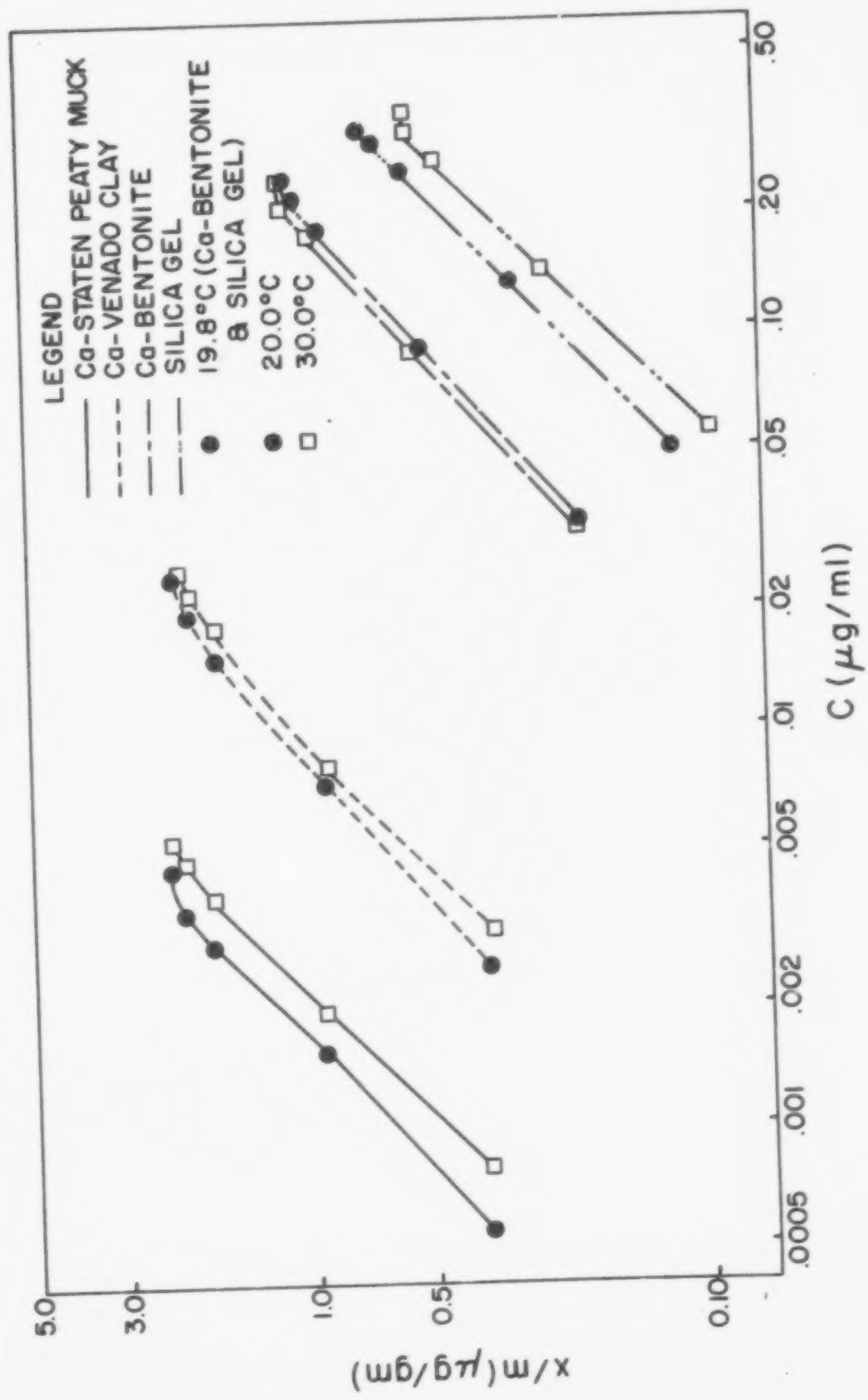


FIGURE 21

ADSORPTION OF β-BHC FROM WATER (LOG-LOG PLOT)



It is interesting to note that, with the exception of the γ-BHC-Venado clay-water system at 10°C, the 1/n values increase uniformly for each adsorbent as temperature increases.

Table 29

Freundlich Constants for the Isotherms

Isomer and solvent	Adsorbent	T (°C)	k	k'	1/n	n
aqueous γ-BHC	Ca-Staten peaty muck	10	377		.956	1.046
		20	331	2630	.969	1.032
		30	269	3350	.981	1.020
		40	197		.983	1.017
	Ca-Venado clay	10	53.8		.866	1.155
		20	45.7	277	.841	1.189
		30	41.3	363	.845	1.183
		40	36.1		.846	1.181
	Ca-bentonite	20	2.92	19.5	.886	1.128
		30	2.71	28.2	.911	1.098
	Silica gel	20	6.88	51.2	.938	1.065
		30	4.62	54.2	.957	1.045
γ-BHC in hexane	Ca-Staten peaty muck	10	0.974	3340	.886	1.128
		20	0.823	6180	.935	1.070
aqueous β-BHC	Ca-Staten peaty muck	20	456	1170	.950	1.053
		30	437	1550	.990	1.010
	Ca-Venado clay	20	62.8	148	.861	1.162
		30	60.2	187	.883	1.132
	Ca-bentonite	19.8	3.96	9.33	.863	1.158
		30	4.46	13.9	.885	1.130
	Silica gel	19.8	2.13	5.60	.971	1.029
		30	1.64	5.80	.985	1.015

This is predicted on the basis of the derivation of the Freundlich equation for dilute solutions given by Kipling (page 36 of this thesis). It was observed that by letting 1/n equal $\frac{RT(x/m)_m}{\sigma_1-\sigma_2}$, equation (24) reduced to the Freundlich equation. One would, therefore, expect 1/n values for the isotherms of the system to relate to one another as the ratio of the corresponding absolute temperatures T_2/T_1. Table 30 shows that, with the exception of the γ-BHC-Venado clay-water system at 10° and 20°C, all the 1/n ratios are within 3.2% of the corresponding T_2/T_1 ratios. This validates the nature of the relationship between absolute temperature and 1/n given by the above equality.

Table 30

Relationship between 1/n Values and Temperature

Isomer and Solvent	T_2 (°C)	T_1 (°C)	$\frac{T_2}{T_1}$ (°K)	$(1/n)_{T_2}/(1/n)_{T_1}$ where $T_2 > T_1$			
				Staten	Venado	Bentonite	Silica gel
aqueous γ-BHC	20	10	1.035	1.013	.972		
	30	20	1.034	1.012	1.005	1.028	1.020
	40	30	1.033	1.002	1.002		
γ-BHC in hexane	20	10	1.035	1.055			
aqueous β-BHC	30	20	1.034	1.042	1.026	1.025	1.014

A consideration of the relationship between 1/n values and temperature leads one to conclude that normal isotherms of the same system for different temperatures will inevitably cross at some equilibrium concentration point since they tend to converge in the lower concentration range. This is strictly true only if the same

1/n values apply to the entire concentration range studied. Thus, the crossing (at about 24 µg/ml equilibrium concentration) of the 10^o and 20^oC isotherms for the γ-BHC-Staten peaty muck-hexane system (figure 16) can be explained on this basis. In the corrected isotherms, since the relative position of the isotherms for a given system is in general completely reversed from that in normal isotherms, corrected isotherms would be expected never to cross, but to diverge throughout the entire concentration range. This is illustrated in figure 15b.

The k and k' values serve as indices of adsorption. They equal the hypothetical x/m values for a constant c or c/c_o value, c and c/c_o equaling unity in the case of k and k', respectively. With the exception of the silica gel-water systems, Table 29 shows higher k values for β-BHC than for γ-BHC. The smaller k values on silica gel for β-BHC compared to γ-BHC may be discussed in relation to the k values for the bentonite-water systems. It appears that because of the zero dipole moment of β-BHC and the consequent absence of any dipole-dipole-type interaction as an adsorptive force, the net adsorptive forces between β-BHC molecules and the adsorbents silica gel and Ca-bentonite are less than those for γ-BHC molecules. The reason why k values for β-BHC decreased with silica gel but increased somewhat with Ca-bentonite relative to γ-BHC may be related to spacial or geometric factors. It may be that once β-BHC molecules are adsorbed between clay layers and possibly between the saturating cations on the oxygen surface of Ca-bentonite, their displacement by water molecules is more difficult than such displacement on the relatively 'unprotected' oxygen surface of silica. So, even though a higher solution fugacity of β-BHC (compared to γ-BHC) provides a greater driving force toward adsorption, the relative ease energetically with which water molecules can displace these β-BHC molecules on most sites on silica gel results in k values lower than those obtained for γ-BHC. The higher k values of β-BHC compared to γ-BHC for the other three adsorbents is probably due primarily to the lower solubility limit of β-BHC and its consequent higher fugacity in solution than γ-BHC at equal concentrations.

The usefulness of the k' values lies in the assumption that while the curves relating fugacity and concentration may vary widely with temperature, solvent, or the isomer used as solute, those relating fugacity and reduced concentration will tend to group closely together or form a single curve. This implies the assumption that it is the position of a particular solute concentration relative to the saturated solubility, which is the factor determining the solute's fugacity in the solvent. The k' values may, consequently, be considered as the hypothetical amount adsorbed from solutions having a nearly constant equilibrium solute fugacity. Since fugacity of the solute in the bulk phase (and therefore in the adsorbed phases) may therefore be considered to be essentially constant, discussion of k' values rules out any consideration of the influence of differing solute fugacities in the bulk phase on adsorption.

As seen in Table 29, values of k' increase with temperature for each system. Even in the cases where no clear difference between the two corrected isotherms could be observed on the graphs, as with the silica gel-water systems, a definite small increase in k' is seen to result from the temperature increase. Since the solute fugacity is considered to be constant here, temperature may have effected such increases through its influence upon the fugacity of the solvent molecules adsorbed on the surface. Comparison of k' values for the γ-BHC-hexane and γ-BHC-water systems containing Ca-Staten peaty muck reveal that the lindane molecule actually competes more effectively with hexane molecules than with water molecules on this adsorbent. This would lead one to conclude that the polar character of γ-BHC may be as important on this adsorbent as we have already assumed to be true on the crystalline adsorbents. It is likely that lindane competes most effectively with hexane for sites on the mineral portion of this soil. Uniformly lower k' values were obtained for β-BHC compared to γ-BHC adsorption from water for corresponding adsorbents. The reason for this would appear to lie in the non-polar character of the β-BHC molecule, and the consequent reduction of ability to compete with water molecules. The lowest k' values (for β-BHC on silica gel) may be explained as was done above in the discussion of the k values.

2. Changes in the standard partial molar thermodynamic properties associated with adsorption

In order to calculate values of $\Delta \bar{G}^o$, values for c_2^s, the concentration of adsorbate on the solid, had to be calculated from the x/m values. Molecular cross-sectional areas for the solute and solvent in each case had to be determined or estimated in order to calculate values of c_2^s. The cross-sectional area for the BHC molecule was estimated as 43.5 $\mathring{A}^2$ by consideration of the bond angles and bond lengths of the molecule. Cross-sectional areas for the three 'sides' of the molecule were estimated, and, since the values for the three areas were close to one another, they were averaged to give the result, 43.5 $\mathring{A}^2$. This value compares well with the value of 44.1 $\mathring{A}^2$ obtained by applying the equation given by Kodera and Onishi[45]

$$A_i = 1.091 \left[(M_i \times 10^{24})/(N\rho) \right]^{2/3}, \qquad (55)$$

where A_i is the molecular cross-sectional area of the adsorbate in square angstroms, M_i is the molecular weight, ρ is the density of adsorbate, and N is Avogadro's number. The values for density used for BHC, nanograde hexane, and water were 1.88, 0.687, and 1.00, respectively. A value for the cross-sectional area of the water molecule has been given by Fu, Hansen, and Bartell[22] as 9.9 $\mathring{A}^2$ and by Thomas[85] as 11.6 $\mathring{A}^2$. In addition, use of equation (55) yields 10.5 $\mathring{A}^2$. The average of these three values, 10.6 $\mathring{A}^2$, was taken as the cross-sectional area of the water molecule. A cross-sectional area for hexane was estimated by applying equation (55) and then correcting the resulting estimate by a factor of 1.202, which was the factor Kodera and Onishi[45] found related the experimentally determined molecular area for n-butane with that calculated from equation (55). The result was a value of 46.1 $\mathring{A}^2$ for hexane.

With the aid of the molecular cross-sectional area for BHC, we can calculate values for c_2^s and also for θ, the fraction of the surface of the adsorbent covered by solute molecules. An expression for θ is given by

$$\theta = \frac{(x/m) N A_2}{s \cdot M_2 \times 10^6}, \qquad (56)$$

where x/m is the amount adsorbed in µg/gm of adsorbent, N is Avogadro's number, A_2 is the cross-sectional area of the solute molecule in cm^2, s is the specific surface of the adsorbent in cm^2/gm, and M_2 is the molecular weight. Table 31 gives the maximum values for θ attained in the isotherm studies of aqueous γ-BHC and β-BHC at 20°C. It is apparent that the surface coverage in these experiments is limited to a very low range ($\theta < 0.01\%$).

Table 31

Some Maximum Surface Coverage Values in Isotherm Studies at 20°C

Isomer and solvent	Venado clay	Staten peaty muck	Bentonite	Silica gel
γ-BHC in water	4.80×10^{-5}	9.43×10^{-5}	9.10×10^{-6}	1.40×10^{-5}
β-BHC in water	4.65×10^{-6}	8.82×10^{-6}	1.22×10^{-6}	0.71×10^{-6}

The concentration of the solute in the adsorbed phase, c_2^s, is defined similarly to the definition employed by Fu, Hansen, and Bartell.[22] c_2^s is the number of µg of solute adsorbed per ml of solvent in contact with the adsorbent surface. This corresponds exactly with the definition of c_2 (elsewhere designated as c in this paper). c_2 is the bulk concentration of solute at equilibrium in µg per ml of solvent. (Because of the very dilute nature of most of the solutions employed it was possible to approximate c_2, thus defined, satisfactorily by using the experimental concentration values in units of µg of solute per ml of solution.) Defined in the above manner c_2^s values were calculated by the expression

$$c_2^s = \frac{(\rho_1/M_1)A_1}{\frac{s}{N(x/m)} - \frac{A_2}{M_2 \times 10^6}} , \tag{57}$$

where ρ_1 is the density of the solvent, M_1 the molecular weight of the solvent, A_1 the cross-sectional area of the solvent molecule in cm^2, s the specific surface of the adsorbent in cm^2 per gram, N Avogadro's number, x/m the amount adsorbed in $\mu g/gm$, A_2 the cross-sectional area of the solute molecule in cm^2, and M_2 the molecular weight of the solute. The derivation of equation (57) is given in the Appendix, and the numerical expression of this equation in terms of x/m for each adsorbent and solvent is presented in Table A-4 of the Appendix.

It was stated on page 44 that because of the way in which the standard states of the solute in the bulk phase and in the adsorbed phase were chosen

$$\lim_{c_2^s \to 0} (c_2^s/c_2) = a_2^s/a_2 = K_o$$

Although we have just defined c_2^s and c_2 somewhat differently from that in the theoretical section the above equality holds equally well. From trial extrapolations of plots of c_2^s/c_2 versus x/m it was apparent that the c_2^s/c_2 ratio tended to rise rapidly as x/m approached zero. Therefore, it was found necessary to plot $\log(c_2^s/c_2)$ versus $(x/m)^n$ for the lowest three isotherm points in order to obtain a linear extrapolation to zero x/m. n represents the power to which the x/m values had to be taken to obtain such a linear plot. The value of n was determined by trial and error and was found to vary widely between systems and even within a given system for different temperatures. With some systems the slopes of the resulting lines at two or more temperatures were fairly comparable. Figure A-4 of the Appendix shows reasonable extrapolated values of log c_2^s/c_2 at four temperatures for the γ-BHC-Staten peaty muck-water system. But for a few systems, such as γ-BHC-bentonite-water, γ-BHC-Staten peaty muck-hexane, and β-BHC-silica gel-water, the difference in the slopes of the extrapolating line for the two temperatures was great. This may be seen in figures A-5, A-6, and A-7 in the Appendix. The resulting great difference in the value of the intercept (log K_o) led to correspondingly high, and unreasonable, values for $\Delta \bar{H}^o$ and $\Delta \bar{S}^o$. The values for $\Delta \bar{G}^o$, $\Delta \bar{H}^o$, and $\Delta \bar{S}^o$ obtained by means of this extrapolation technique are given in Table A-5 of the Appendix.

Because of obtaining such unreasonable values through the use of the extrapolation method, the writer decided to adopt another method for determining K_o. (K_o is the thermodynamic equilibrium constant shown to be closely approximated by K_2 for dilute solutions. K_2 is defined by $K_2 = a_2^s/a_2$.) It was necessary to choose as K_o the ratio of c_2^s/c_2 obtained for the lowest concentration point of each isotherm. This involved the assumption that from the lowest equilibrium experimental point to the origin, the isotherm is linear, and, therefore, the c_2^s/c_2 ratio is constant. This is a reasonable assumption considering the very low equilibrium concentrations at the initial point, and in view of equation (14). Further, out of the 22 isotherms, eight yielded (by the aforementioned extrapolation method) log K_o values very close to the log c_2^s/c_2 values of the respective initial experimental points.

The values for $\Delta \bar{G}^o$, $\Delta \bar{H}^o$, and $\Delta \bar{S}^o$ are presented in Table 32. $\Delta \bar{G}^o$ values were determined from the c_2^s/c_2 ratios of the initial experimental points which were then substituted for K_o in equation (31). $\Delta \bar{H}^o$ was calculated according to equation (33). Values of $\Delta \bar{S}^o$ were determined from equation (34). In the case of Staten peaty muck and Venado clay in γ-BHC-water systems, since there were values of $\Delta \bar{G}^o$ for four temperatures, $\Delta \bar{S}^o$ was also determined from equation (35). The chord-area method was used to plot the curves of $\Delta \bar{S}^o$ versus temperature (figure 22). The two methods of determining $\Delta \bar{S}^o$ are seen to yield values which agree well. But as pointed out on page 45, such agreement cannot be assumed to indicate a high level of accuracy for the values. Values for $\Delta \bar{H}^{o'}$ and $\Delta \bar{S}^{o'}$, representing the solubility-corrected values for $\Delta \bar{H}^o$ and $\Delta \bar{S}^o$, respectively, are given in Table 33. $\Delta \bar{H}^{o'}$ values were determined from equation (47) and $\Delta \bar{S}^{o'}$ values from equation (34). In the latter equation $\Delta \bar{H}^{o'}$ was substituted for $\Delta \bar{H}^o$, and $\Delta \bar{G}^o_{av}$ was the same as shown in Table 32.

In comparing and interpreting the 'uncorrected' quantities it is important to realize that, as defined, they represent the difference between the particular differential thermodynamic quantity for the solute at the standard state in the adsorbed phase and the corresponding quantity for the solute at the standard state in the bulk solution. Thus, $\Delta \bar{G}^o = \bar{G}_2^{o,s} - \bar{G}_2^o$, and $\Delta \bar{S}^o = \bar{S}_2^{o,s} - \bar{S}_2^o$, etc. The definition of the 'corrected' change in standard enthalpy ($\Delta \bar{H}^{o'}$) involves four terms rather than only two. The 'corrected' enthalpy change was shown in the theoretical section (p. 56) to be obtained by adding the heat of solution, $\Delta \bar{H}_s$, to the differential heat of adsorption. Thus, in this case, we have

Table 32

Values of $\Delta \bar{G}^o$, $\Delta \bar{H}^o$, and $\Delta \bar{S}^o$ associated with Adsorption

System	Temp. (°C)	K_o	log K_o	$\Delta \bar{G}^o$	$\Delta \bar{H}^o$	Average $\Delta \bar{G}^o$	$\Delta \bar{S}^{o*}$	$\Delta \bar{S}^{o/}$
γ-BHC-Ca-Staten peaty muck-water	10	7819	3.89313	-5,040				
					-3,600	-5,070	5.10	-
	20	6285	3.79833	-5,100				
					-5,470	-5,090	-1.29	-1.27
	30	4610	3.66374	-5,080				
					-5,950	-5,070	-2.86	-2.73
	40	3364	3.52681	-5,050				
γ-BHC-Ca-Venado clay-water	10	986.2	2.99396	-3,880				
					-64.9	-3,950	13.5	12.9
	20	982.3	2.99225	-4,010				
					-2,430	-4,040	5.41	5.10
	30	856.2	2.93256	-4,070				
					-3,150	-4,080	3.04	2.94
	40	724.6	2.86012	-4,100				
γ-BHC-Ca-bentonite-water	20	18.72	1.27221	-1,710				
					-2,960	-1,680	-4.29	
	30	15.82	1.19935	-1,660				
γ-BHC-Silica gel-water	20	33.93	1.53062	-2,050				
					-8,420	-1,940	-21.7	
	30	21.07	1.32367	-1,840				
γ-BHC-Ca-Staten peaty muck-hexane	10	11.63	1.06545	-1,380				
					-4,000	-1,330	-9.27	
	20	9.12	0.96003	-1,290				
β-BHC-Ca-Staten peaty muck-water	20	10,280	4.01189	-5,380				
					-6,680	-5,360	-4.41	
	30	7,042	3.84771	-5,340				
β-BHC-Ca-Venado clay-water	20	1,200	3.07909	-4,130				
					-3,990	-4,130	0.463	
	30	956.9	2.98088	-4,130				
β-BHC-Ca-bentonite-water	19.8	27.49	1.43914	-1,930				
					753	-1,980	9.16	
	30	28.71	1.45805	-2,020				
β-BHC-Silica gel-water	19.8	9.29	0.96819	-1,300				
					-5,540	-1,220	-14.5	
	30	6.75	0.82915	-1,150				

* Calculated from equation (34).

/ Calculated from equation (35).

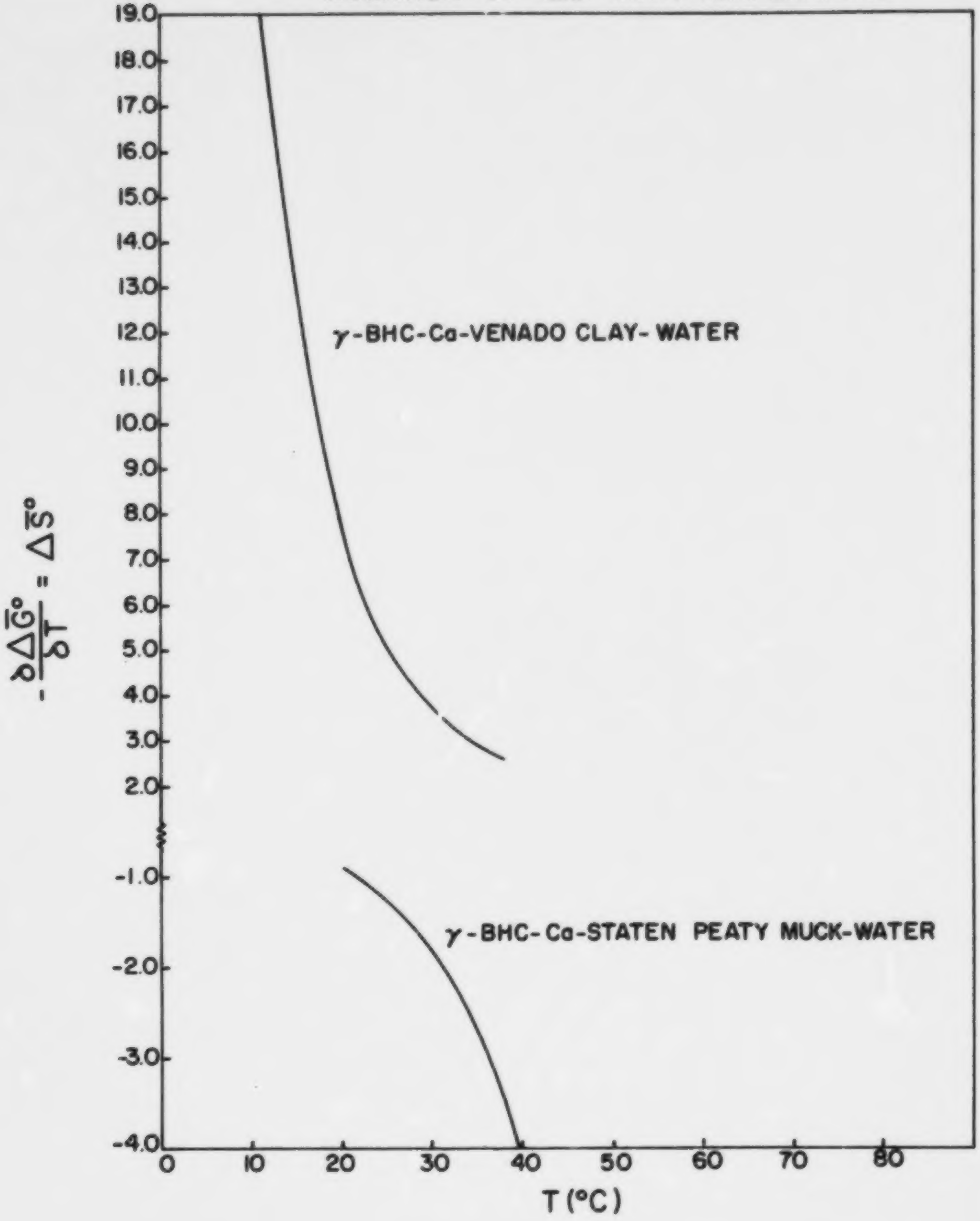
Table 33

Values of $\Delta \bar{H}^{o\prime}$ and $\Delta \bar{S}^{o\prime}$

System	Temp. (^{o}C) range	$\log \frac{(c_o)_{T_2}}{(c_o)_{T_1}}$	$\log \frac{(c_o\ K)_{T_2}}{(c_o\ K)_{T_1}}$	$\Delta \bar{H}^{o\prime}$	$\Delta \bar{G}^{o}$ (average)	$\Delta \bar{S}^{o\prime}$
γ-BHC-Ca-Staten peaty muck-water	20-30	.18808	.05349	2,180	-5,090	24.4
γ-BHC-Ca-Venado Clay-water	20-30	.18808	.12839	5,220	-4,040	31.1
γ-BHC-Ca-bentonite-water	20-30	.18808	.11522	4,690	-1,680	21.4
γ-BHC-Silica gel-water	20-30	.18808	-.01887	-767	-1,940	3.95
γ-BHC-Ca-Staten peaty muck-hexane	10-20	.15594	.05052	1,920	-1,330	11.3
β-BHC-Ca-Staten peaty muck-water	20-30	.12613	-.03805	-1,550	-5,360	12.8
β-BHC-Ca-Venado clay-water	20-30	.12613	.02792	1,140	-4,130	17.7
β-BHC-Ca-bentonite-water	20-30	.12613	.14504	5,780	-1,980	26.0
β-BHC-Silica gel-water	20-30	.12613	-.01291	-514	-1,220	2.38

FIGURE 22

VARIATION OF $\Delta\bar{S}°$ WITH TEMPERATURE



$$\Delta \bar{H}^{o\prime} = \Delta \bar{H}^{o} + \Delta \bar{H}_s.$$

Thus, $$\Delta \bar{H}^{o\prime} = \bar{H}_2^{o,s} - \bar{H}_2^{o} + \bar{H}_2 - \bar{H}_s.$$

The standard partial molar enthalpy of the solute in the bulk phase, $\bar{H}_2^{o}$, is the partial molar enthalpy of a solution at infinite dilution. Since the solutions employed in this research were very dilute it can be considered that $\bar{H}_2 \cong \bar{H}_2^{o}$. Thus, $\Delta \bar{H}^{o\prime} \cong \bar{H}_2^{o,s} - \bar{H}_s$, where $\bar{H}_2^{o,s}$ is the partial molar heat content of the adsorbed solute in its standard state, and $\bar{H}_s$ is the molar enthalpy of the pure solid solute. Now, $\Delta \bar{S}^{o\prime}$ is determined by the expression,

$$\Delta \bar{S}^{o\prime} = \frac{\Delta \bar{H}^{o\prime} - \Delta \bar{G}^{o}_{av}}{T_{av}}.$$

Only in an approximate way is it, therefore, possible to equate $\Delta \bar{S}^{o\prime}$ with the difference between the partial molar entropy of the adsorbed solute in its standard state ($\bar{S}_2^{o,s}$) and the molar entropy of the pure solid solute ($\bar{S}_s$).

$$\Delta \bar{S}^{o\prime} \approx \bar{S}_2^{o,s} - \bar{S}_s.$$

Comparison of $\Delta \bar{G}^{o}$ values for the different systems leads one to note that the relative order of the systems with respect to the magnitude of $\Delta \bar{G}^{o}$ values is the same as that with respect to the Freundlich constant k, with one exception. The $\Delta \bar{G}^{o}$ values for the γ-BHC-Staten peaty muck-hexane system are comparable to the values for the β-BHC-silica gel-water system, while the k values of the former system are less than half of those for the latter one. The range of $\Delta \bar{G}^{o}$ values is from -1.15 kcal/mole, for the β-BHC-silica gel-water system, to -5.38 kcal/mole, for the β-BHC-Staten peaty muck-water system. The relationship between $\Delta \bar{G}^{o}$ and temperature is not uniform. In any case, it is apparent that $\Delta \bar{G}^{o}$ for all systems is not greatly affected by temperature. (The difference for any ten-degree change amounting to 200 cal/mole or less.)

Values of $-\Delta \bar{H}^{o}$ for the γ-BHC-water systems containing Staten peaty muck and Venado clay are seen to increase significantly as temperature increases. This fact throws some doubt on our use of the integrated form of the Van't Hoff equation (equation 35). That is, the accuracy of the $\Delta \bar{H}^{o}$ values thus obtained is less than if the temperature coefficient of $\Delta \bar{H}^{o}$ had been lower. From Table 32 it is evident that, with the exception of the β-BHC-bentonite system, all the $\Delta \bar{H}^{o}$ values are negative, indicating lower partial molar heat content of the adsorbed solute in its standard state compared to that for the solute in its standard state in solution. This implies that attractive forces operating at the solid-solution surface have effected a lower heat content of the BHC molecule relative to that in solution. In contrast, Table 33 shows that, with three exceptions, the $\Delta \bar{H}^{o'}$ values are positive, which indicates that the partial molar enthalpies for the adsorbed solute in its standard state are greater than the molar enthalpies of the pure solid solute. Such positive $\Delta \bar{H}^{o'}$ values indicate the presence of weaker attractive forces in the adsorbed state relative to that in pure solid BHC.

It is interesting to observe that the three systems which yielded negative $\Delta \bar{H}^{o'}$ values are the very systems which we assumed had essentially no heat content changes on the basis of the near superimposition of the corrected isotherms in figures 12b, 13b, and 14b (γ-BHC-Silica gel, β-BHC-Staten peaty muck, and β-BHC-Silica gel aqueous systems). The positive values for $\Delta \bar{H}^{o'}$ range from 1.14 to 5.78 kcal/mole. The $\Delta \bar{H}^{o'}$ values for the two γ-BHC-Staten peaty muck systems (aqueous and hexane) do not differ greatly (2.18 compared to 1.92 kcal/mole). At first glance one would expect these values to correspond closely, provided the assumptions involved in the derivation of equation (47) hold. Because it would seem that

$$(\bar{H}_2^{o,s})_{\substack{\text{in}\\ \text{hex}}} - \bar{H}_s \cong (\bar{H}_2^{o,s})_{\substack{\text{in}\\ \text{water}}} - \bar{H}_s.$$

But the correspondence of the two $\Delta \bar{H}^{o'}$ values may well be fortuitous, for $(\bar{H}_2^{o,s})_{\substack{\text{in}\\ \text{hexane}}}$ may differ significantly from $(\bar{H}_2^{o,s})_{\substack{\text{in}\\ \text{water}}}$. A primary reason for this would be that on the average the γ-BHC molecules very possibly occupy quite different sites on the peaty muck in the aqueous system relative to the hexane system.

Discussion of changes in the standard partial molar entropy would best be focused upon the $\Delta \bar{S}^{o'}$ values. In this way, solubility effects may be ignored. The reason for all the values for $\Delta \bar{S}^{o'}$ being positive must lie in the increased number of degrees of freedom of the solute in the adsorbed state relative to the pure solid state. Even with the almost inevitable lack of translational freedom and the existence of some polar orientation of the solute molecules adsorbed on the adsorbent, the number of rotational and vibrational degrees of freedom in the adsorbed state undoubtedly exceeds those available to the solute in the solid state. It is apparent from a consideration of $\Delta \bar{S}^{o}$ values in Table 32 that for some systems (those having negative $\Delta \bar{S}^{o}$ values) the number of degrees of freedom is less for the adsorbed solute than for the solute dissolved in the bulk solution in its standard state.

Returning to Table 33 we see that the lowest $\Delta \bar{S}^{o'}$ values for both γ- and β-BHC are found in the silica gel systems. It would appear that the two BHC isomers adsorbed on silica gel most nearly approach the degree of order (lack of probable degrees of freedom) of the pure solid. This could indicate a considerable degree of orientation of the adsorbed molecules on the silica surface, or some other type of immobilization of the molecules such as to reduce their freedom. The γ-BHC molecules adsorbed from water on Venado clay, Staten peaty muck, and bentonite, by contrast, appear to have considerable freedom, including possibly some translational freedom.

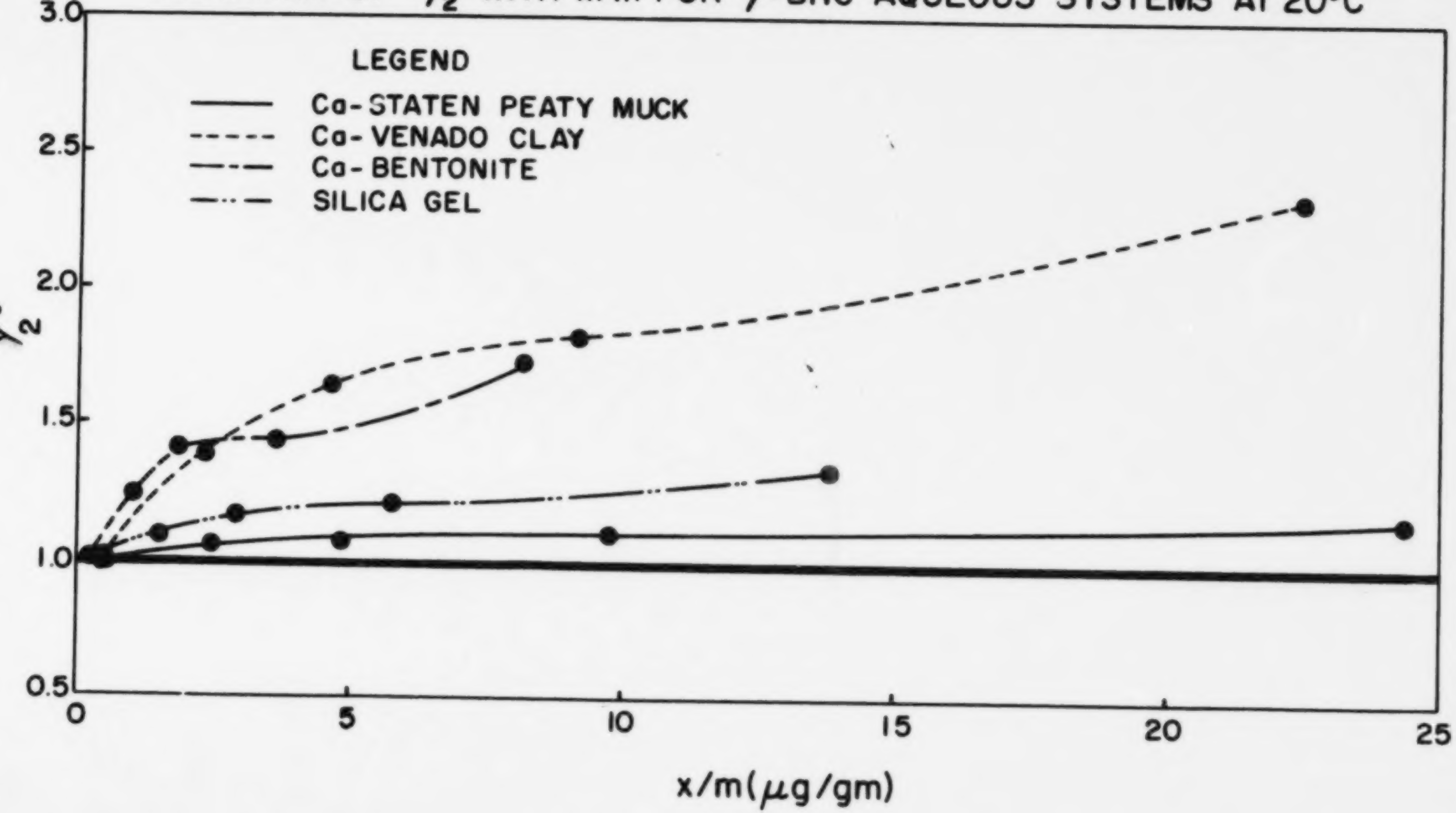
In the case of Venado clay and Staten peaty muck there is a considerably lower degree of freedom of the adsorbed β-BHC molecules compared to that for aqueous γ-BHC. The lower $\Delta \bar{S}^{o'}$ value for γ-BHC on Staten peaty muck adsorbed from hexane relative to that for γ-BHC adsorbed on the same soil from water may indicate that the water molecules are more mobile on this adsorbent than are the hexane molecules. Consequently, more degrees of freedom would be allowed the adsorbed BHC molecules in an aqueous medium than in a hexane medium.

3. Determination of surface activity coefficients (γ_2^s)

Using the values of K_o determined from the initial experimental point for each isotherm, values of γ_2^s were computed from equation (36), which is $\gamma_2^s = K_o(a_2/c_2^s)$. It was necessary to substitute c_2 values for a_2 in this equation. Thus, calculated values for γ_2^s deviate from the true values by a factor of γ_2 which may differ noticeably from unity in the upper part of the concentration range. The calculated values for γ_2^s are given in Table A-6 of the Appendix. Figure 23 shows

FIGURE 23

VARIATION OF γ_2^s WITH x/m FOR γ-BHC AQUEOUS SYSTEMS AT 20°C



plots of γ_2^s versus x/m for the four adsorbents in aqueous γ-BHC solutions at 20°C. It is apparent from this graph that γ-BHC behaves most ideally on Ca-Staten peaty muck and least so on Ca-Venado clay. It is possible that some association of adsorbed γ-BHC molecules has begun to occur on Venado clay, but not to any great extent on Staten peaty muck. A similar difference, but of less magnitude, is observed for these two adsorbents in the case of β-BHC adsorption. (See figure A-8.)

4. Changes in differential enthalpy and entropy at constant interfacial tension

Values for $\Delta \bar{H}_\sigma$ and $\Delta \bar{H}'$ at four or more magnitudes of total surface free energy change ($A_T \Delta\sigma$) were calculated from equations (41) and (46), respectively. (A_T represents the total surface area of the adsorbent in the flask, and $\Delta\sigma$ is the change in interfacial tension accompanying adsorption.) As described in connection with equation (41) it was necessary to calculate a value for the total surface energy change ($A_T \Delta\sigma$) for each experimental point by means of the Gibbs equation. Then, values of m_2^s/m_2, or $(m_2^s/m_2)m_o$, were calculated for each point. Plots of $A_T \Delta\sigma$ versus m_2^s/m_2 (or $\left[m_2^s/m_2\right]m_o$) were made for each isotherm. Then, for different temperatures of the same system m_2^s/m_2 values at constant values of $A_T \Delta\sigma$ were read off the graphs, and the $\Delta \bar{H}_\sigma$ values were calculated directly.

The calculation of $A_T \Delta\sigma$ values was performed in the following manner. The Gibbs adsorption equation for dilute solutions may be expressed as

$$\Delta\sigma = - R T \int_0^a \Gamma_2 \, d\ln a. \qquad (58)$$

Now, we shall assume that $m \cong a$, where m is the molality in moles solute per 1000 grams of solvent. Also, we assume that for dilute solutions

$$\Gamma_2 = n_2^*/A_T,$$

where n_2^* is the total number of moles of solute transferred from the bulk solution to the adsorbed phase during adsorption, and A_T is the total surface area of the amount of adsorbent in the system. Then the total free energy change at the surface is $A_T\,\Delta\sigma$ and

$$A_T\,\Delta\sigma = -\,R\,T\int_0^m n_2^*\,d\ln m. \tag{59}$$

Now,

$$n_2^* = \frac{(x/m)(5) \times 10^{-6}}{M_2} \tag{60}$$

where x/m is the number of micrograms of solute per gram of adsorbent transferred from the bulk solution to the solid surface, 5 is the number of grams of adsorbent in the system, 10^{-6} is the number of grams per microgram, and M_2 is the molecular weight of the solute. Further, for dilute solutions

$$m \cong \frac{c \times 10^{-3}}{M_2\,\rho_{SOLN}} \tag{61}$$

where c is the equilibrium bulk concentration in mg/l, 10^{-3} is the number of grams/mg., and ρ_{SOLN} is the density of the solution. Then,

$$dm = \frac{dc}{\rho_{SOLN} M_2 \times 10^3}\,. \tag{62}$$

Substituting equations (60), (61), and (62) into equation (59), we have

$$A_T \Delta\sigma = - R T \int_0^c \frac{5 \times 10^{-6}(x/m)}{M_2 c} dc$$

$$A_T \Delta\sigma = - \frac{5 \times 10^{-6}}{M_2} R T \int_0^c \frac{(x/m)}{c} dc.$$

Now, for the isotherms, or portions of isotherms, which yield linear log-log plots, $x/m = kc^{1/n}$. Thus,

$$A_T \Delta\sigma = - \frac{5 \times 10^{-6}}{M_2} R T \int_0^c \frac{kc^{1/n}}{c} dc$$

and $$A_T \Delta\sigma = - \frac{5 \times 10^{-6}}{M_2} R Tk \left[\frac{1}{(1/n)} c^{1/n} \Big|_0^c \right]$$

The result is

$$A_T \Delta\sigma = - \frac{(5 \times 10^{-6})RTkn}{M_2} c^{1/n}. \qquad (63)$$

By means of equation (63) the values of $-A_T \Delta\sigma$ were calculated for each isotherm. The calculation of these values is summarized in Table A-7 of the Appendix.

Values of m_2^s/m_2 were calculated assuming that the volume of the adsorbed layer was negligible. Thus,

$$m_2^s/m_2 = \frac{5(x/m)}{25(c\ )} = \frac{kc^{1/n}}{5c},$$

where 5 is the number of grams of adsorbent and 25 the number of milliliters of solution in each system. From Table A-7 the values of $-A_T\,\Delta\sigma$ were plotted against values of m_2^s/m_2 and $(m_2^s/m_2)m_o$. Examples of such plots are shown in figures 24a, 24b, 25a, and 25b. The remaining such plots are presented in figures A-9 through A-11 in the Appendix. In general, the relative positions of the constant-temperature curves for a given system are reversed when $-A_T\,\Delta\sigma$ is plotted against $(m_2^s/m_2)m_o$ rather than m_2^s/m_2. For the systems demonstrating near superimposition of the isotherms in the plots of x/m vs. c/c_o (figures 12b, 13b, and 14b), we find that the $-A_T\,\Delta\sigma$ versus $(m_2^s/m_2)m_o$ curves intersect at some point. (See, for example, figure 25b). This, of course, results in a change in sign of the calculated $\Delta\,\bar{H}'$ values. All the curves exhibit a similar shape. The shape of the curves shows that as the surface coverage, or $-A_T\,\Delta\sigma$ values, becomes small, the ratio m_2^s/m_2 tends to increase more and more. At higher surface coverages, m_2^s/m_2 values change only slightly with changes in $-A_T\,\Delta\sigma$.

In figures 26, 27, and 28 the variation of $\Delta\,\bar{H}_\sigma$ with a function of surface coverage $(-A_T\,\Delta\sigma)$ is shown graphically for each system. Figure 29 shows the variation of $\Delta\,\bar{H}'$ with $-A_T\,\Delta\sigma$. It may be noteworthy that $\Delta\,\bar{H}_\sigma$ in figure 28 (the γ-BHC-Staten peaty muck-hexane system) declines rapidly with an increase in surface free energy, while the curve for the γ-BHC-Staten peaty muck-water system (fig. 26) descends very gradually. The cause of this difference may lie in the nature of the sites on which γ-BHC is adsorbed on this adsorbent from the two solvents. One can imagine that γ-BHC molecules in an aqueous medium would tend to adsorb on sites in the organic fraction while in a hexane medium they perhaps would tend to adsorb more on the inorganic fraction.

FIGURE 24a

VARIATION OF $-A_T\,\Delta\sigma$ WITH (m_2^s/m_2) FOR AQUEOUS γ-BHC SYSTEMS

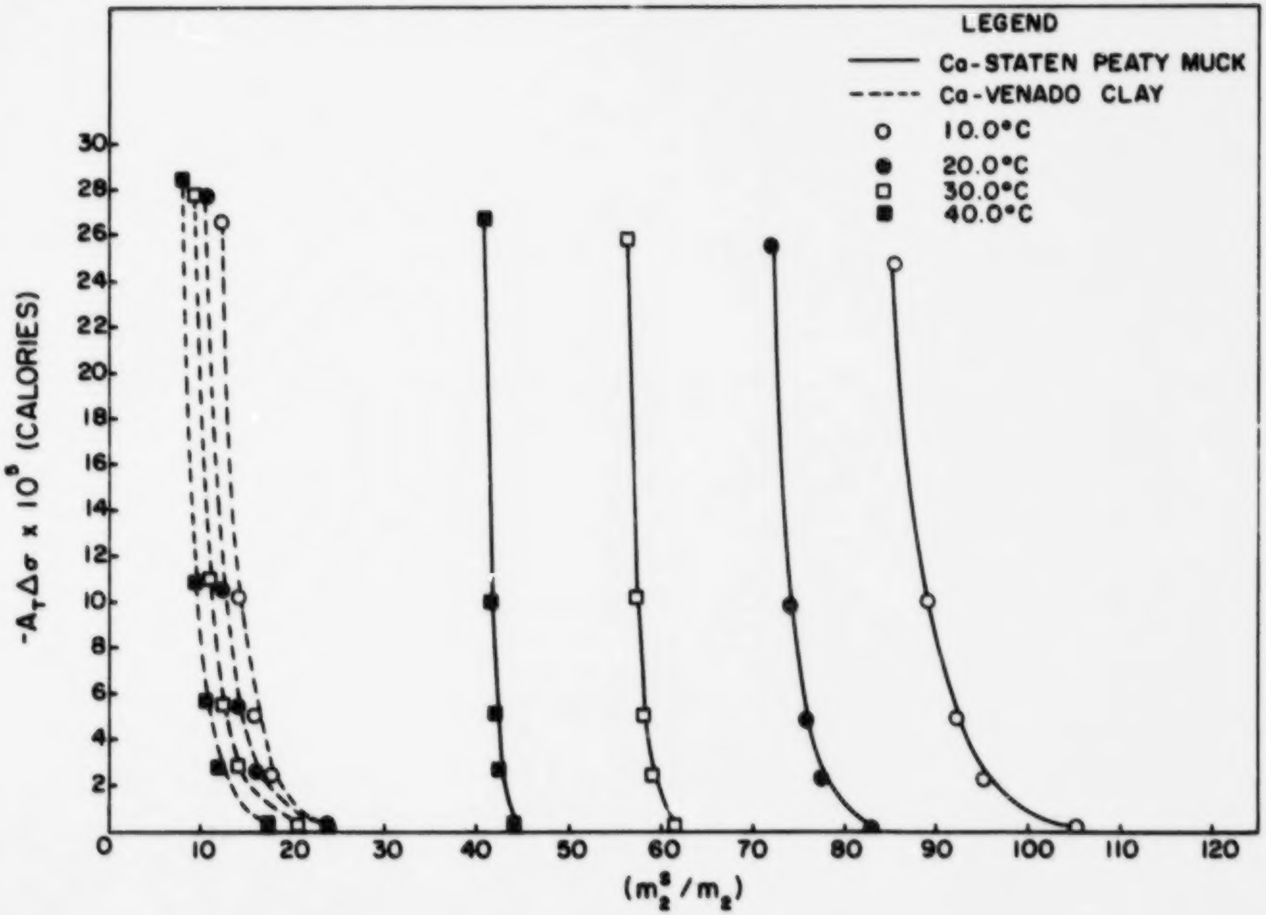


FIGURE 24b

VARIATION OF $-A_T \Delta\sigma$ WITH $(m_2^s/m_2)\,m_0$ FOR AQUEOUS γ-BHC SYSTEMS

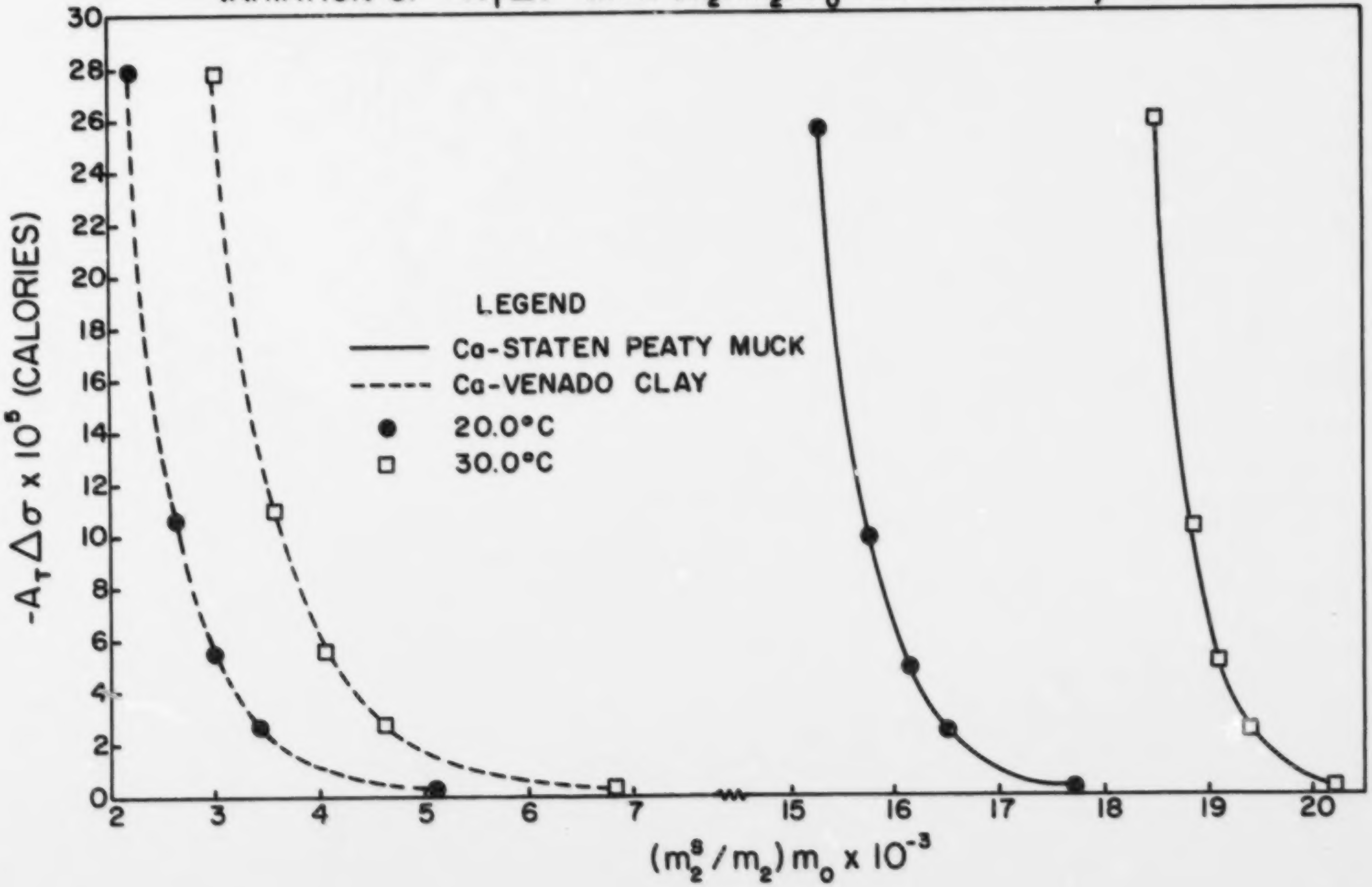


FIGURE 25a

VARIATION OF $-A_T \Delta\sigma$ WITH (m_2^s/m_2) FOR AQUEOUS γ-BHC SYSTEMS

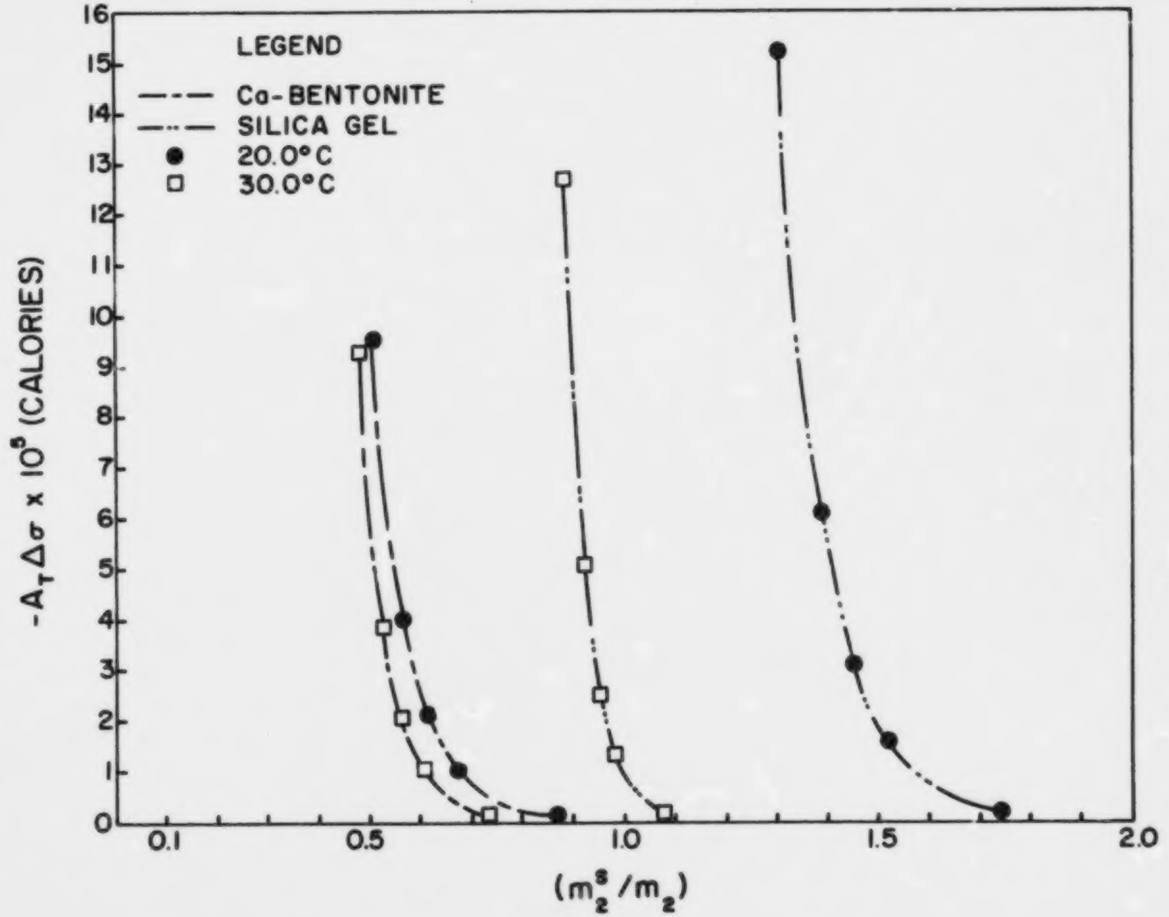


FIGURE 25b

VARIATION OF $-A_T \Delta\sigma$ WITH $(m_2^s/m_2)m_0$ FOR AQUEOUS γ-BHC SYSTEMS

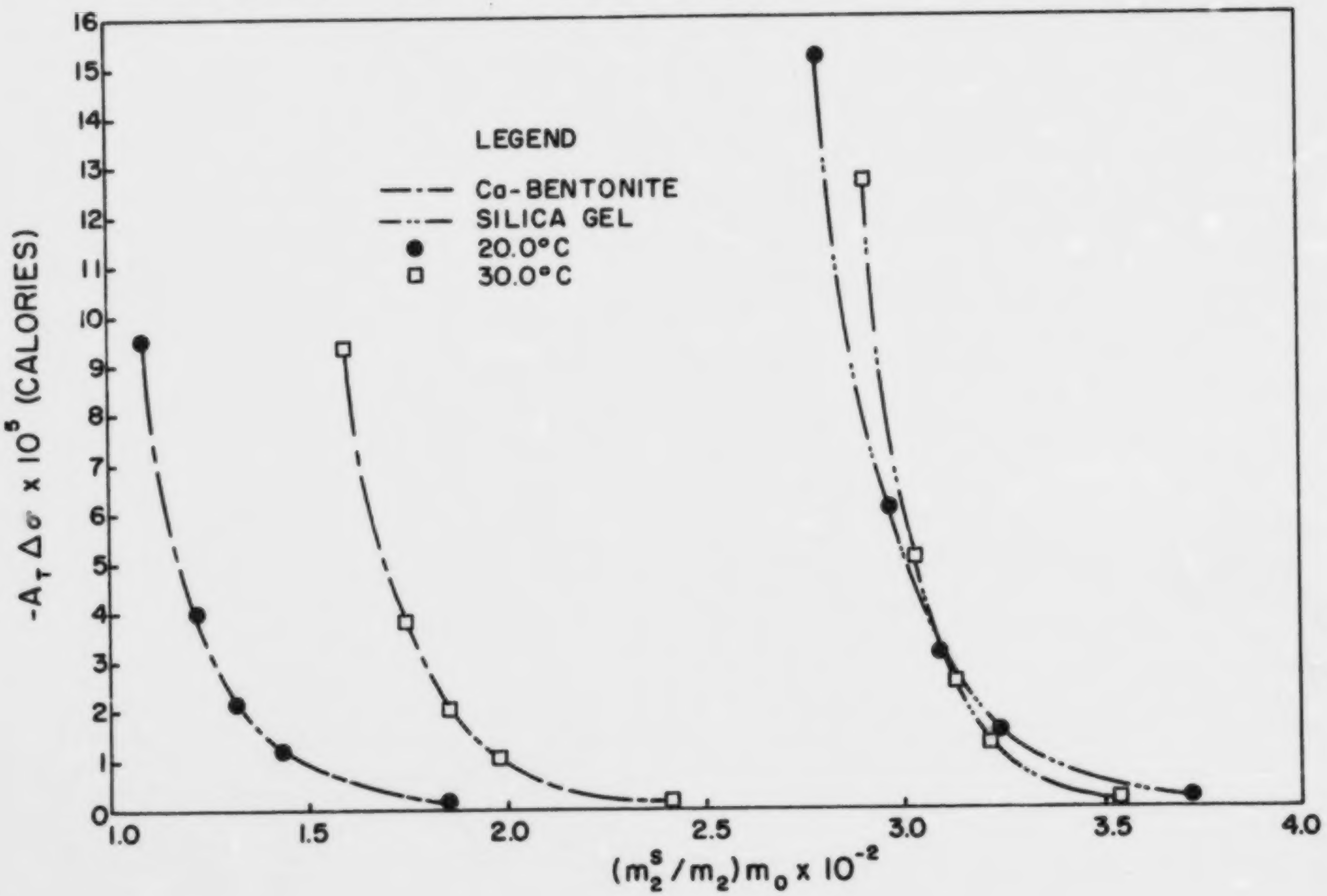


FIGURE 26

VARIATION OF $\Delta\overline{H}_\sigma$ (25°C) WITH A FUNCTION OF SURFACE COVERAGE

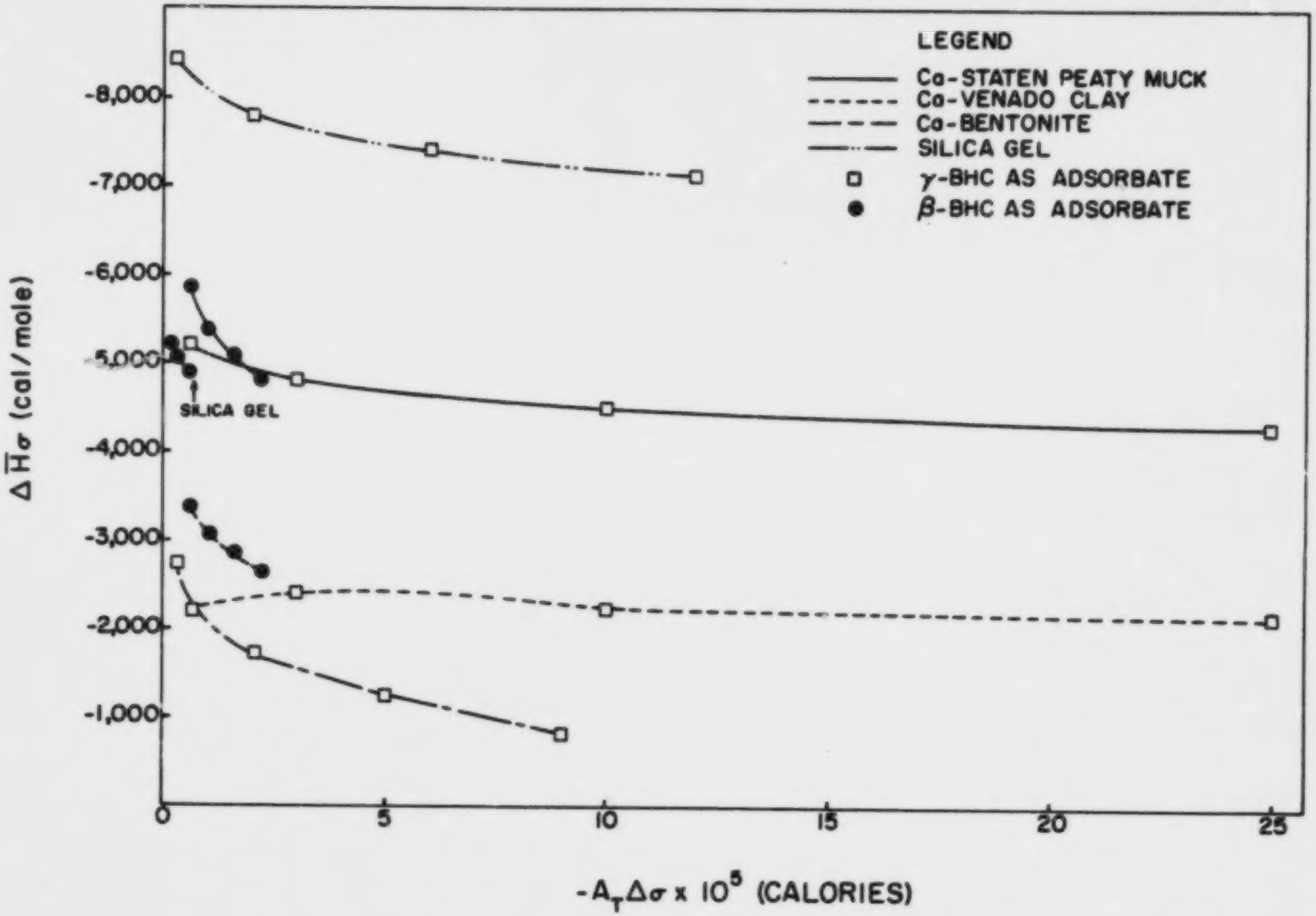


FIGURE 27

VARIATION OF $\Delta\bar{H}_\sigma$ AT THREE TEMPERATURES WITH A FUNCTION OF SURFACE COVERAGE FOR TWO AQUEOUS γ-BHC SYSTEMS

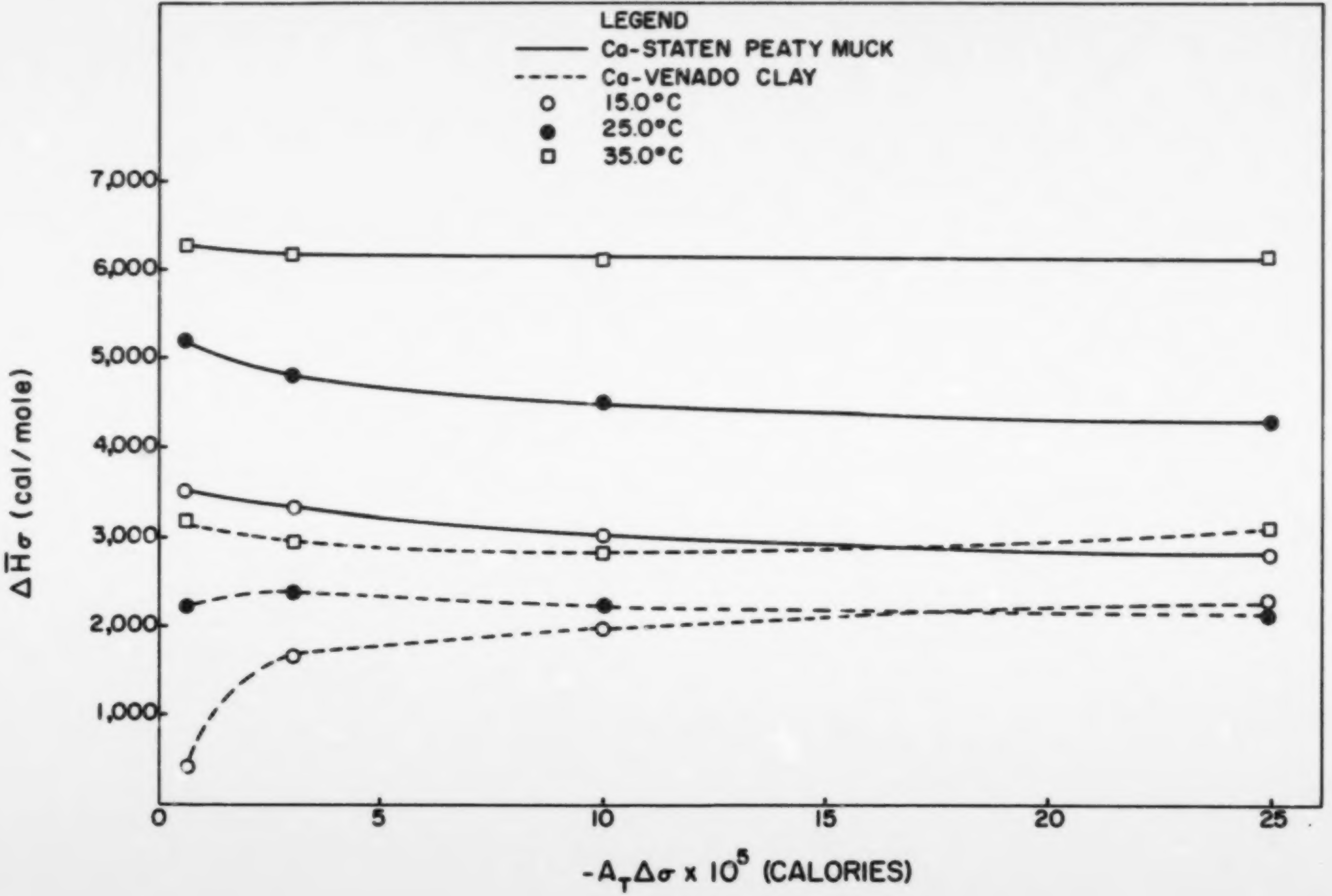
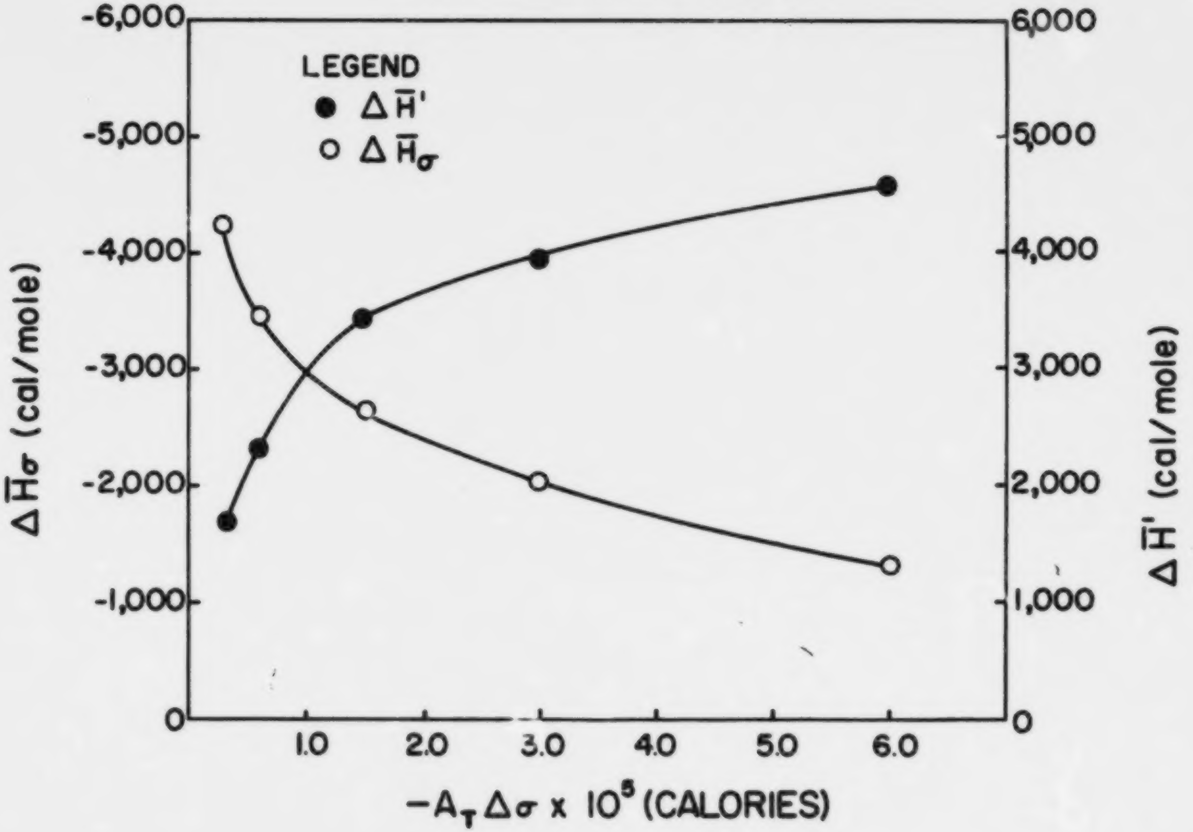


FIGURE 28

VARIATION OF $\Delta\overline{H}$ (15°C) WITH A FUNCTION OF SURFACE COVERAGE (γ-BHC- STATEN MUCK- HEXANE SYSTEM)



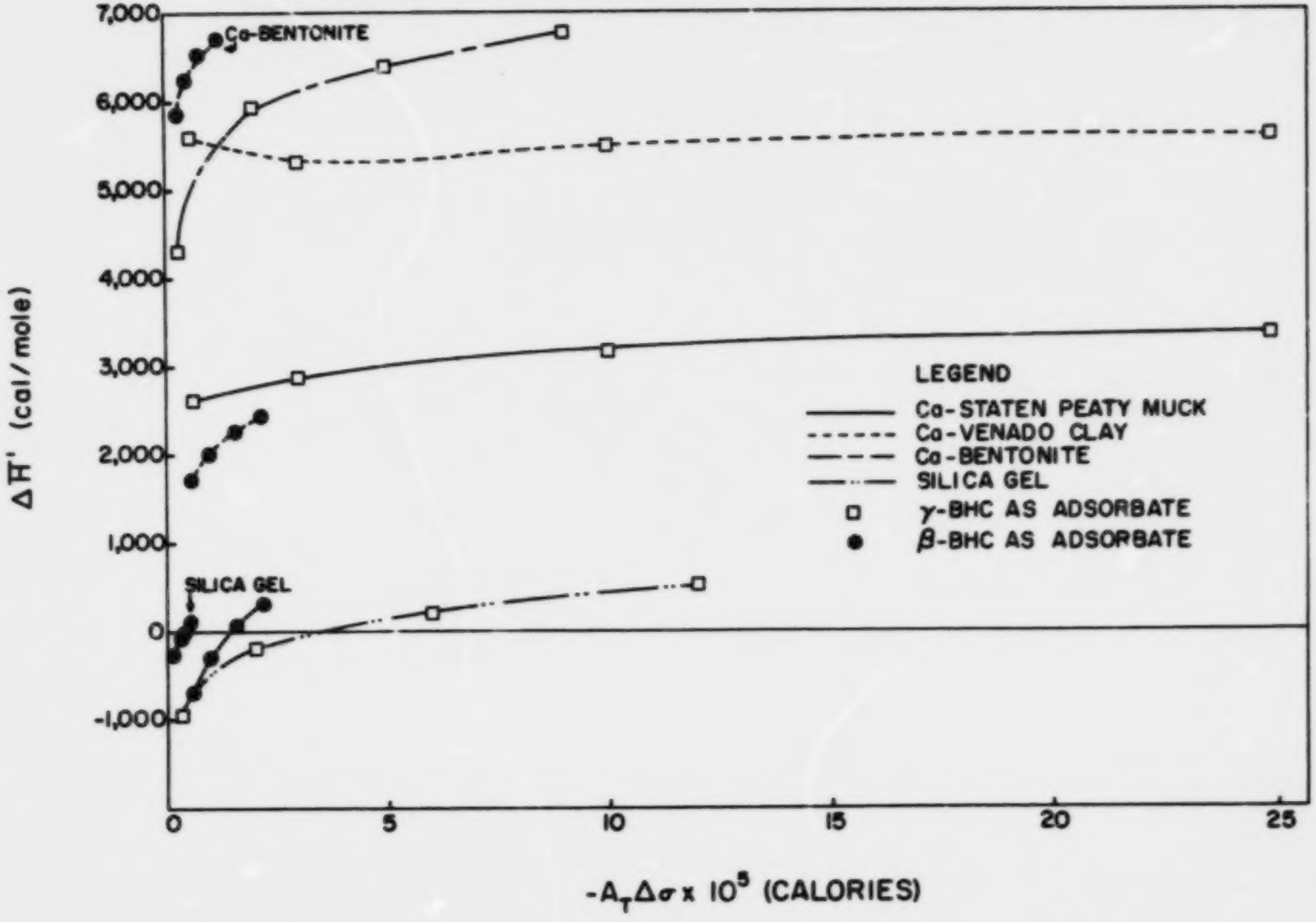
On the basis of this hypothesis, it appears from the graphs of the two systems (hexane and water) that in the low range of surface coverage studied, site energies vary significantly in the inorganic fraction, but only slightly in the organic fraction of Staten peaty muck. This conclusion appears to be confirmed further by the definite decline in the curves for silica gel and bentonite in figure 26. These adsorbents, representing two types of soil inorganic fractions, apparently have a greater range of site energies for lindane adsorbed from water, than do Staten peaty muck and Venado clay. In the latter adsorbents organic matter obviously is important for providing adsorption sites for lindane in water.

The curves in figure 27, showing the change of $\Delta \bar{H}_{\sigma}$ with surface coverage at several temperatures, indicate a more or less constant displacement downward as temperature decreases, but essentially no change in the shape of the curves for the two adsorbents in γ-BHC-water systems. The lower (15°C) curve for Venado clay is not reliable because it is based in part on the data for the γ-BHC-Venado clay-water system at 10°C, which was observed earlier to be aberrant with respect to the 1/n Freundlich value.

Figure 29 shows that the curves for aqueous β-BHC are somewhat higher than those for aqueous γ-BHC in the case of silica gel and Ca-bentonite. While the curves for aqueous β-BHC on Venado clay and Staten peaty muck are in a definitely lower $\Delta \bar{H}'$ range than those for aqueous γ-BHC. One can attempt an explanation by assuming initially that there is a higher molar enthalpy for β-BHC in the pure solid state than for solid γ-BHC. The energy of γ-BHC in the solid state could be considered to be lower than β-BHC because of the higher intermolecular

FIGURE 29

VARIATION OF $\Delta \overline{H}'$ (25°C) WITH A FUNCTION OF SURFACE COVERAGE



attraction between the molecules of the former. If this assumption is made, then one is led to conclude from the curves in figure 29 that the energy of β-BHC adsorbed on silica gel or bentonite is a great deal more than for γ-BHC on the same adsorbents. It is possible, further, that since the non-polar portions of the organic fractions may provide sites for both aqueous β-BHC and γ-BHC on Venado clay and Staten peaty muck, the energy of the β-BHC isomer adsorbed on these adsorbents may be roughly the same as that of the γ-BHC isomer. These conclusions can perhaps be best elucidated through the use of the hypothetical graphs in figure 30. These represent plausible interpretations of the curves in figure 29. The magnitude of $\bar{H}_s$ for γ-BHC and for β-BHC is shown to be constant for all three adsorbent systems.

At the constant coverage to which figure 30 applies there is an extremely high affinity of the surface of silica gel for γ-BHC molecules. But at higher surface coverages figure 29 shows that the average affinity is reduced. And at $-A_T \Delta\sigma = 12 \times 10^{-5}$ calories the partial molar enthalpy of adsorbed γ-BHC molecules is 500 calories greater than the molar enthalpy of pure solid lindane. A similar phenomenon occurs in the case of β-BHC adsorption from water on silica gel and Staten peaty muck.

The calculated values of $\Delta \bar{H}_\sigma$ and $\Delta \bar{H}'$ are presented in Tables 34 and 35, together with values for $\Delta \bar{S}_\sigma$ and $\Delta \bar{S}'$, respectively. These changes in partial molar entropy were determined from the relation $\Delta \bar{H}_\sigma = T \Delta \bar{S}_\sigma$, and $\Delta \bar{H}' = T \Delta \bar{S}'$, which hold for any point on an isotherm. Isosteric heats (Q_Γ) were also determined. These were calculated by obtaining values for equilibrium concentrations at two temperatures at a constant x/m value and then applying

FIGURE 30

POSSIBLE RELATIONSHIPS BETWEEN $\overline{H}_2^S$ AND $\overline{H}_S$ FOR AQUEOUS β-BHC AND γ-BHC FOR THREE ADSORBENTS

($-A_T \Delta\sigma = 1 \times 10^{-5}$ CALORIES)

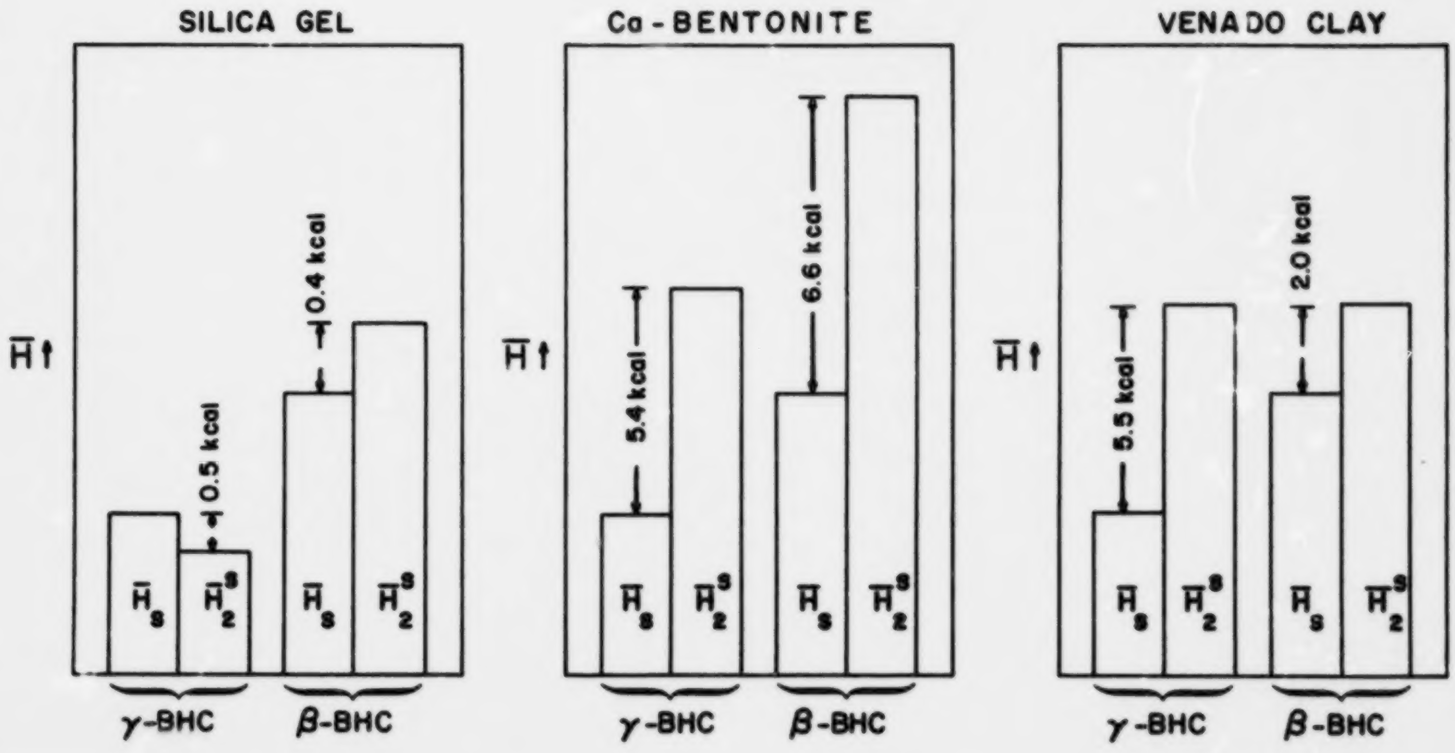

SILICA GEL
Ca - BENTONITE
VENADO CLAY
$\overline{H}$ ↑
$\overline{H}_s$
$\overline{H}_2^s$
0.5 kcal
0.4 kcal
5.4 kcal
6.6 kcal
5.5 kcal
2.0 kcal
γ-BHC
β-BHC

Table 34

Constant Interfacial Tension Heats and Entropy Changes in Adsorption ($\Delta \bar{H}_\sigma$ and $\Delta \bar{S}_\sigma$) (in calories/mole and calories/deg-mole)

System	Chosen $-A_T\,\Delta\sigma$ x 10^5	15°C		25°C		35°C	
		$\Delta \bar{H}_\sigma$	$\Delta \bar{S}_\sigma$	$\Delta \bar{H}_\sigma$	$\Delta \bar{S}_\sigma$	$\Delta \bar{H}_\sigma$	$\Delta \bar{S}_\sigma$
γ-BHC-	0.6	-3,510	-12.2	-5,210	-17.5	-6,250	-20.3
Ca-Staten	3	-3,320	-11.5	-4,810	-16.1	-6,170	-20.0
peaty muck-	10	-3,040	-10.5	-4,510	-15.1	-6,120	-19.8
water	25	-2,810	- 9.76	-4,300	-14.4	-6,160	-20.0
γ-BHC-	0.6	- 440	- 1.52	-2,220	- 7.45	-3,170	-10.3
Ca-Venado	3	-1,690	- 5.87	-2,390	- 8.02	-2,950	- 9.56
clay-	10	-1,980	- 6.84	-2,240	- 7.50	-2,830	- 9.19
water	25	-2,280	- 7.90	-2,140	- 7.19	-3,080	- 9.98
γ-BHC-	0.3			-2,760	- 9.25		
Ca-bentonite-	2			-1,700	- 5.70		
water	5			-1,260	- 4.23		
	9			- 845	- 2.83		
γ-BHC-	0.3			-8,430	-28.3		
Silica gel-	2			-7,810	-26.2		
water	6			-7,410	-24.8		
	12			-7,140	-23.9		
γ-BHC-	0.3	-4,240	-14.7				
Ca-Staten	0.6	-3,450	-12.0				
peaty muck-	1.5	-2,640	- 9.18				
hexane	3.0	-2,030	- 7.04				
	6.0	-1,300	- 4.52				
β-BHC-	0.6			-5,840	-19.6		
Ca-Staten	1.0			-5,390	-18.1		
peaty muck-	1.6			-5,080	-17.0		
water	2.2			-4,810	-16.1		
β-BHC-	0.6			-3,380	-11.3		
Ca-Venado	1.0			-3,060	-10.2		
clay-	1.6			-2,860	- 9.60		
water	2.2			-2,650	- 8.90		
β-BHC-	0.3			1,000	3.37		
Ca-bentonite-	0.5			1,260	4.22		
water	0.8			1,590	5.33		
	1.2			1,680	5.65		
β-BHC-	0.15			-5,220	-17.5		
Silica gel-	0.30			-5,050	-17.0		
water	0.40			-5,080	-17.0		
	0.55			-4,900	-16.4		

Table 35

'Corrected' Constant Interfacial Tension Heats of Adsorption
($\Delta \bar{H}'$) and entropy changes ($\Delta \bar{S}'$)
(in calories/mole and calories/deg-mole)

System	Chosen $-A_T\ \Delta\sigma$ $\times 10^5$	$\Delta \bar{H}'$ (25°)	$\Delta \bar{S}'$ (25°C)
γ-BHC-	0.6	2,640	8.84
Ca-Staten peaty	3	2,860	9.60
muck-	10	3,180	10.6
water	25	3,350	11.2
γ-BHC-	0.6	5,600	18.8
Ca-Venado clay-	3	5,340	17.9
water	10	5,510	18.5
	25	5,580	18.7
γ-BHC-	0.3	4,320	14.5
Ca-bentonite-	2	5,930	19.9
water	5	6,390	21.4
	9	6,780	22.7
γ-BHC-	0.3	- 945	-3.17
Silica Gel-	2	- 174	-0.58
water	6	211	0.71
	12	522	1.75
γ-BHC-	0.3	1,690	5.85
Ca-Staten peaty	0.6	2,310	8.03
muck-	1.5	3,430	11.9
hexane	3.0	3,960	13.7
	6.0	4,580	15.9
β-BHC-	0.6	- 688	-2.31
Ca-Staten peaty	1.0	- 283	-0.95
muck-water	1.6	65.1	0.22
	2.2	315	1.06
β-BHC-	0.6	1,730	5.81
Ca-Venado clay-	1.0	2,030	6.82
water	1.6	2,280	7.66
	2.2	2,450	8.23
β-BHC-	0.3	5,870	19.7
Ca-bentonite-	0.5	6,260	21.0
water	0.8	6,520	21.9
	1.2	6,710	22.5
β-BHC-	0.15	- 225	-0.75
Silica Gel-	0.30	- 57.4	-0.19
water	0.40	0.00	0.00
	0.55	104	0.35

the equation for Q_Γ given on page 47. These are reported in Table 36. Comparison of Tables 34 and 36 show that for each system the Q_Γ values are of the same order of magnitude as the $\Delta \bar{H}_\sigma$ values. But a fact that might offer discouragement to the use of isosteric heats for approximating the $\Delta \bar{H}$ of adsorption is that in five cases the trend of the Q_Γ values with increasing surface coverage is different or reversed from the trend of the $\Delta \bar{H}_\sigma$ values. Thus, although the order of magnitude of $\Delta \bar{H}_\sigma$ at a given surface coverage can be reasonably estimated for these systems by the isosteric heat, the direction of change of $\Delta \bar{H}_\sigma$ with surface coverage cannot be estimated with assurance by means of Q_Γ values.

A consideration of the $\Delta \bar{S}'$ values in Table 35 reveal that, with the exception of the γ-BHC-Venado clay-water system, the values of $\Delta \bar{S}'$ increase steadily with increasing surface coverage. This is fully understandable when one recognizes that $\Delta \bar{S}' = \bar{S}_2^s - \bar{S}_s$, where $\bar{S}_2^s$ is the partial molar entropy of the solute in the adsorbed phase and $\bar{S}_s$ is the molar entropy of the solute in the pure, undissolved solid state We have already discussed why entropy would ordinarily increase in the transfer of dn moles of solute from the pure solid state to the adsorbed state. There is obviously less order in most adsorbed states compared to that in the pure solid state. But also it can be recognized that the number of degrees of freedom of the adsorbed molecules on the average would tend to increase relative to the solid state as surface coverage increases. Assuming a range of site energies for the adsorbent, with increased coverage the adsorbed molecules would tend to approach the number of degrees of freedom possessed by the solute molecules in the bulk solution. Ordinarily one would expect at equilibrium that

Table 36

Isosteric Heats of Adsorption (Q_{Γ}) (in calories/mole)

System	Chosen x/m (μg/gm)	Q_{Γ} (15°)	Q_{Γ} (25°)	Q_{Γ} (35°)
γ-BHC-Ca-Staten peaty muck-water	5	-2,760	-4,740	-5,290
	10	-3,030	-4,720	-5,360
	15	-3,090	-4,700	-5,680
	20	-3,140	-4,440	-6,010
γ-BHC-Ca-Venado clay-water	5	-1,500	-2,600	-2,460
	10	-1,810	-2,870	-2,280
	15	-2,150	-2,770	-2,500
	20	-2,530	-2,230	-3,110
γ-BHC-Ca-bentonite-water	1		-1,980	
	3		-1,620	
	5		-1,510	
	7		-1,370	
γ-BHC-Silica gel-water	2		-7,960	
	4		-7,520	
	6		-7,450	
	8		-7,440	
	10		-7,320	
γ-BHC-Ca-Staten peaty muck-hexane	0.5	-3,120		
	2	-1,420		
	4	-1,470		
	6	-1,530		
β-BHC-Ca-Staten peaty muck-water	0.8		-4,330	
	1.2		-4,270	
	1.6		-4,590	
	2.0		-5,240	
β-BHC-Ca-Venado clay-water	0.6		-3,920	
	1.0		-3,750	
	1.2		-3,640	
	1.6		-3,410	
	1.8		-3,210	
β-BHC-Silica gel-water	0.2		-4,590	
	0.3		-4,290	
	0.4		-4,380	
	0.5		-4,770	

there would exist the greatest freedom for the solute molecules in the bulk solution rather than in the adsorbed state. Reference to Table 34 shows indeed that, with the exception of the β-BHC-bentonite-water system, all the $\Delta \bar{S}\sigma$ values ($\bar{S}_2^s - \bar{S}_2$) are negative. β-BHC molecules apparently possess a much greater number of degrees of freedom and/or a greater magnitude of configurational entropy when adsorbed on Ca-bentonite compared to the other adsorbents. High values for $\bar{S}_2^s$ may also be deduced from the high values of $\Delta \bar{S}'$ for γ-BHC adsorption from water on Ca-Venado clay and Ca-bentonite. A high degree of order in the adsorbed state is indicated by the low values for $\Delta \bar{S}'$ when γ-BHC or β-BHC is adsorbed on silica gel.

5. Integral free energies and integral heats of adsorption

As discussed in the theoretical section, the integral free energy of adsorption (ΔG) may be considered to include two separate terms -- ΔG^B, the change in free energy of a system due to the lowering of the bulk concentration, and ΔG^a, the change in the free energy of the solution-solid interface. Now, for each system we have already calculated several values for ΔG^a in connection with the procedure employed to determine $\Delta \bar{H}_\sigma$ values. For, ΔG^a is identical with the quantity $A_T \Delta\sigma$. Therefore, to calculate ΔG, it was necessary only to calculate ΔG^B according to equation (49), and add to it the appropriate value for ΔG^a. Values for ΔG^B were calculated for each experimental point. These integral quantities are presented in Table 37. For the highest surface coverages* ΔG values range from -1.19×10^{-5}

---

* Because only the five lowest points were used to calculate the equation for the isotherm in the case of the γ-BHC-Staten peaty muck-hexane system, values for the highest surface coverage of this system are not included.

Table 37

Integral Free Energies of Adsorption

Ca-Staten peaty muck

Isomer and Solvent	Temperature (^{o}C)	Initial conc. (μg/ml)	$-\Delta G^{B}$ (cal.) x 10^{5}	$-\Delta G^{a}$ (cal.) x 10^{5}	$-\Delta G$ (cal.) x 10^{5}
γ-BHC in water	10	.09902	2.501	0.284	2.785
		.4951	11.07	2.35	13.42
		.9911	21.76	4.92	26.68
		1.9804	42.85	10.18	53.03
		4.953	106.67	24.94	131.61
	20	.09887	2.478	0.285	2.763
		.4943	10.80	2.52	13.32
		.9896	21.63	4.94	26.56
		1.9773	42.86	9.99	52.85
		4.9445	105.75	25.68	131.43
	30	.09862	2.402	0.291	2.693
		.4930	10.52	2.50	13.02
		.9870	20.84	5.14	25.98
		1.9723	41.51	10.27	51.78
		4.9321	103.09	25.94	129.03
	40	.09828	2.308	0.293	2.601
		.4914	9.82	2.71	12.53
		.9837	19.92	5.11	25.03
		1.9656	39.81	10.08	49.89
		4.915	97.38	26.91	124.29
β-BHC in water	20	.074	1.82	0.386	2.20
		.191	4.60	1.03	5.63
		.362	8.76	1.86	10.62
		.425	10.23	2.23	12.46
	30	.074	1.74	0.390	2.13
		.191	4.53	0.956	5.49
		.361	8.52	1.84	10.36
		.425	9.91	2.27	12.18
γ-BHC in hexane	10	.1017	0.110	0.115	0.225
		.5087	0.507	0.487	0.994
		1.0174	0.901	0.918	1.819
		3.0479	2.28	2.49	4.77
		10.174	7.01	7.32	14.33
	20	.1004	0.090	0.087	0.177
		.5022	0.387	0.401	0.788
		1.0044	0.769	0.767	1.54
		3.0087	2.28	2.14	4.42
		10.044	6.59	6.74	13.33

Table 37 (cont.)

Integral Free Energies of Adsorption

Ca-Venado Clay

Isomer and Solvent	Temperature (^{o}C)	Initial conc. (μg/ml)	$-\Delta G^{B}$ (cal.) x 10^{5}	$-\Delta G^{a}$ (cal.) x 10^{5}	$-\Delta G$ (cal.) x 10^{5}
γ-BHC in water	10	.09902	1.810	0.308	2.118
		.4951	7.12	2.49	9.61
		.9911	13.62	5.09	18.71
		1.9804	26.08	10.28	36.36
		4.953	60.85	26.63	87.48
	20	.09887	1.87	0.325	2.19
		.4943	7.13	2.67	9.80
		.9896	13.48	5.47	18.95
		1.9773	25.96	10.64	36.60
		4.9445	59.23	27.90	87.13
	30	.09862	1.86	0.329	2.19
		.4930	7.01	2.74	9.75
		.9870	13.27	5.58	18.85
		1.9723	25.40	10.98	36.38
		4.9321	58.79	27.86	86.65
	40	.09828	1.83	0.335	2.17
		.4914	6.80	2.80	9.60
		.9837	12.87	5.68	18.55
		1.9656	24.94	10.86	35.80
		4.915	56.44	28.53	84.97
β-BHC in water	20	.074	1.25	.424	1.67
		.191	3.13	1.05	4.18
		.362	5.76	1.98	7.74
		.425	6.60	2.42	9.02
	30	.074	1.21	0.431	1.64
		.191	3.14	0.992	4.13
		.361	5.60	2.03	7.64
		.425	6.52	2.42	8.94

Table 37 (cont.)

Integral Free Energies of Adsorption

Ca-bentonite

Isomer and Solvent	Temperature (^oC)	Initial conc. (µg/ml)	$-\Delta G^B$ (cal.) x 10^5	$-\Delta G^a$ (cal.) x 10^5	$-\Delta G$ (cal.) x 10^5
γ-BHC in water	20	.09887	0.593	0.147	0.740
		.4943	1.30	1.11	2.41
		.9896	2.35	2.14	4.49
		1.9774	4.61	4.00	8.61
		4.9446	9.95	9.53	19.48
	30	.09862	0.574	0.134	0.708
		.4931	1.20	1.05	2.25
		.9871	2.31	2.02	4.33
		1.9723	4.50	3.83	8.33
		4.9320	9.72	9.32	19.04
β-BHC in water	19.8	.074	0.301	0.240	0.541
		.191	0.714	0.577	1.29
		.362	1.27	1.04	2.31
		.425	1.43	1.22	2.65
	30	.074	0.321	0.248	0.569
		.191	0.776	0.602	1.38
		.361	1.38	1.10	2.48
		.425	1.62	1.28	2.90

Silica gel

Isomer and Solvent	Temperature (^oC)	Initial conc. (µg/ml)	$-\Delta G^B$ (cal.) x 10^5	$-\Delta G^a$ (cal.) x 10^5	$-\Delta G$ (cal.) x 10^5
γ-BHC in water	20	.09887	0.780	0.191	0.971
		.4943	2.33	1.57	3.90
		.9896	4.48	3.11	7.59
		1.9774	8.72	6.09	14.81
		4.9446	20.31	15.24	35.55
	30	.09862	0.665	0.156	0.822
		.4931	1.75	1.32	3.07
		.9871	3.51	2.56	6.07
		1.9723	6.71	5.11	11.82
		4.9320	15.84	12.72	28.56
β-BHC in water	19.8	.074	0.142	0.120	0.262
		.191	0.352	0.307	0.659
		.362	0.661	0.574	1.23
		.425	0.790	0.666	1.46
	30	.074	0.112	0.100	0.212
		.191	0.293	0.252	0.545
		.361	0.543	0.475	1.02
		.425	0.631	0.560	1.19

calories for aqueous β-BHC on silica gel to -132×10^{-5} calories for aqueous γ-BHC on Staten peaty muck. It is evident, then, that the integral free energy changes occurring as a result of adsorption in the systems employed were of a very low magnitude. The relative contribution of ΔG^B to ΔG was almost always at least as large as ΔG^a and was usually larger. For the aqueous systems with Ca-Staten peaty muck and Ca-Venado clay ΔG^B constituted 70-90% of ΔG, while for the silica gel and Ca-bentonite aqueous systems, as well as for the Staten peaty muck-hexane system, ΔG^B contributed only 48-60% of the total value of ΔG.

For the aqueous γ-BHC systems with Staten peaty muck and Venado clay, since values for ΔG were obtained for four temperatures, values for ΔS were obtained by determining the values of the partial derivative $\left(\frac{\partial \Delta G}{\partial T}\right)_P$. This was done by the chord-area method for each initial solution level. Then, values for ΔH, the integral enthalpy of adsorption, were determined from the ΔG and ΔS values at each level. These quantities are presented in Table 38. A great deal of weight cannot be placed on the ΔS values, because compounding of initial errors result from the fact that these data are several operations removed from the original raw data. Nevertheless, the ΔS values for 30° and 40° for both adsorbents show an expectable steady increase in the negative values with increased final surface coverage. The values of ΔH at 20° and 30°C are plotted against x/m for both adsorbents in figure 31. Essentially linear plots are seen to result. Higher heats are involved in the process of adsorbing aqueous γ-BHC on Staten peaty muck than on Venado clay. The heats evolved apparently increase with temperature rise. This is shown both in figure 31 as well as for all four temperatures in Table 38.

Table 38

Integral Thermodynamic Properties of Adsorption - for γ-BHC-water systems

Ca-Staten Peaty Muck

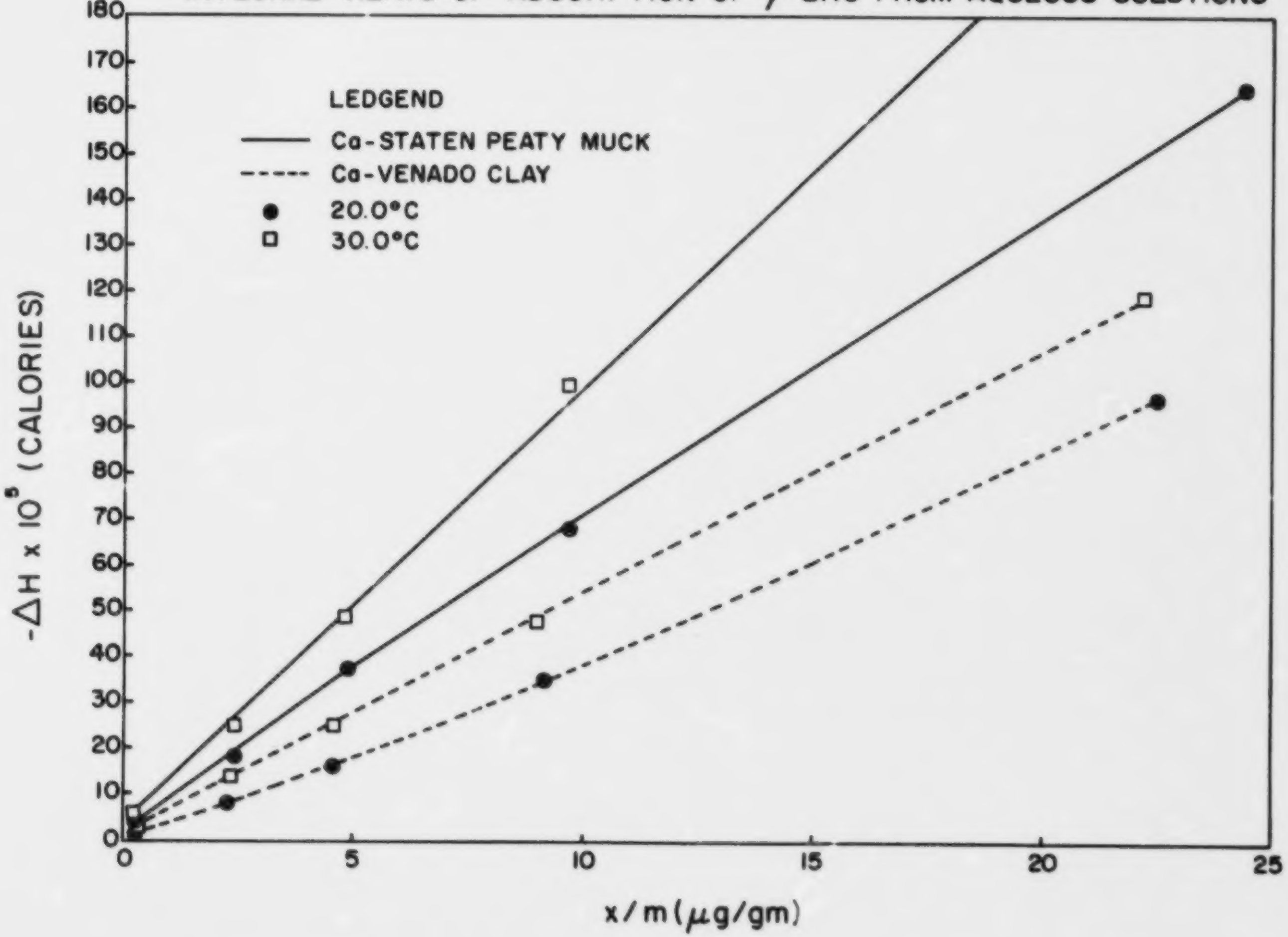
Temp. (^oC)	x/m	-Δ G x 10^5 (cal.)	-Δ S x 10^5 (cal./deg)	-Δ H x 10^5 (cal.)
10	.274	2.78	.0004	2.90
	2.45	13.42	-.004	12.28
	4.90	26.68	-.003	25.84
	9.79	53.03	-.004	51.89
	24.5	131.61	-.043	119.44
20	.273	2.76	.004	3.94
	2.44	13.32	.017	18.31
	4.88	26.56	.036	37.12
	9.75	52.85	.052	68.10
	24.38	131.43	.110	163.68
30	.271	2.69	.008	5.12
	2.43	13.02	.039	24.84
	4.85	25.98	.077	49.33
	9.70	51.78	.158	99.68
	24.23	129.03	.345	233.62
40	.269	2.60	.013	6.67
	2.40	12.53	.075	36.02
	4.81	25.03	.126	64.49
	9.61	49.89	.213	116.59
	23.98	124.29	.610	315.31

Ca-Venado Clay

Temp. (^oC)	x/m	-Δ G x 10^5 (cal.)	-Δ S x 10^5 (cal./deg)	-Δ H x 10^5 (cal.)
10	.265	2.12	-.014	-1.85
	2.35	9.61	-.036	-0.58
	4.66	18.71	-.040	7.39
	9.25	36.36	-.045	23.62
	22.8	87.48	-.002	86.92
20	.265	2.19	-.003	1.31
	2.33	9.80	-.005	8.33
	4.62	18.95	-.009	16.31
	9.17	36.60	-.005	35.14
	22.46	87.13	.034	97.10
30	.263	2.19	.002	2.80
	2.31	9.75	.012	13.38
	4.57	18.85	.021	25.21
	9.04	36.38	.039	48.20
	22.20	86.65	.107	119.09
40	.260	2.17	.003	3.11
	2.27	9.60	.017	14.92
	4.49	18.55	.058	36.71
	8.91	35.80	.092	64.60
	21.71	84.97	.233	157.94

FIGURE 31

INTEGRAL HEATS OF ADSORPTION OF γ-BHC FROM AQUEOUS SOLUTIONS



SUMMARY AND CONCLUSIONS

The adsorptive behavior of γ-BHC and β-BHC in solution was studied by means of laboratory equilibrium experiments. Analysis both by liquid scintillation counting of the tagged solutions and by electron-capture gas chromatography was performed.

Initial adsorption studies of lindane adsorbed from solution were performed prior to the isotherm studies. It was found that the soil, Ca-Venado clay, had to be heated prior to the addition of solutions of lindane in benzene in order to obtain positive adsorption of lindane from benzene. Possibly the sites on which the water thus driven off was held had a specific affinity for lindane relative to benzene. Adsorption of γ-BHC from aqueous solutions on H_2O_2-treated Ca-Venado clay (high in montmorillonite) was about 90% of that on the untreated soil, while adsorption on Ca-bentonite was only about 45% of that on the untreated soil. It was concluded that the portion of the organic matter not readily removed by the peroxide treatment is probably adsorbed strongly on the clay surface and offers much greater affinity for lindane adsorption from water than does the bare clay surface.

A significant degree of probable isomerization at room temperature of γ-BHC and β-BHC in aqueous solutions was observed by gas chromatography in the determination of the solubility of these isomers in water. But essentially no isomerization was observed in the same solution systems in the course of the adsorption experiments. There is no clear explanation for such a discrepancy, but the cause may be related to the saturated state of the solutions in the former case.

Some decomposition of lindane in benzene and hexane solutions in the course of the initial adsorption experiments was observed. Decomposition was concluded to have occurred when the equilibrium concentration of the bulk solution determined by liquid scintillation was significantly higher than that obtained by gas chromatographic analysis. Verification of decomposition was provided by the appearance of peaks of decomposition products on the gas chromatogram. Virtually total decomposition of γ-BHC occurred in benzene and hexane solutions on basic and neutral alumina and on magnesium hydroxide. Peaks for the presumed final and intermediate decomposition products appeared on the chromatograms of these systems. The presumed intermediate product peak also appeared when the adsorbent was Venado clay, although decomposition was relatively low in this case. Some positive relationship between pH of an adsorbent in distilled water and its ability to catalyze γ-BHC decomposition in benzene or hexane media was observed. But, it was concluded, ease with which hydroxyl groups could ionize at the surface in these organic solvents varied greatly between adsorbents. This was considered most critical in determining the extent of lindane decomposition.

A series of adsorption experiments were performed at 20°C to determine the relative adsorbability of lindane on several adsorbents from four solvents -- benzene, hexane, ethanol, and water. In general, the extent of lindane adsorption from the solvents increased in the following order: ethanol < benzene < hexane < water. With the exception of the position of the ethanol systems, the order follows that for decreasing solubility of lindane. The adsorption of γ-BHC on the peaty muck soil was nil from benzene and relatively low from hexane. The highest degree of adsorption of lindane from these two solvents was on silica gel and Venado clay. Apparently the organic solvent molecules compete with γ-BHC most effectively for sites on organic 'surfaces' and least effectively on inorganic oxygen and hydroxyl surfaces. The importance of γ-BHC's dipole nature in adsorption is indicated here.

Since no positive adsorption of lindane on inorganic surfaces from ethanol solutions was observed, one might conclude that it was the polar nature of the ethanol molecules which allowed them to compete successfully with the γ-BHC molecules. The combination of the ethanol molecule's polarity and its organophilic character, in addition to the relatively high solubility of lindane in this solvent apparently acted to bring about almost no positive adsorption of lindane from ethanol solutions.

While the order of the adsorbents with respect to relative adsorption of γ-BHC was almost the same for benzene and hexane solutions, the order was completely changed in adsorption of lindane from aqueous solutions. Highest adsorption of aqueous γ-BHC was on Staten peaty muck, a cation exchange resin, Venado clay, and an anion exchange resin, in decreasing order. Significant but lower adsorption occurred on silica gel, bentonite, and Oakley sand. It was concluded that lindane competes extremely well for adsorption sites on organic matter or organic matrixes. But water, also being polar, offers more effective competition for sites on the inorganic oxygen or hydroxyl surfaces. It is felt by the writer that in the absence of the high fugacity of lindane in aqueous solutions (due to the limited solubility of γ-BHC in water) little or no lindane adsorption would occur on such crystalline surfaces. Comparison of the polarizabilities of lindane and that of each solvent indicated that this property was not of primary importance in the adsorption of γ-BHC from the four solvents. The data indicate a definite role of dipole-dipole interactions in lindane adsorption with the possibility of dispersion forces also being important.

A desorption experiment in connection with the adsorption of γ-BHC from hexane was performed. The results gave tentative support to a belief that lindane adsorption under the given experimental conditions is fully reversible.

Isotherm studies of the adsorption of γ- and β-BHC were carried out using four adsorbents, Ca-Staten peaty muck, Ca-Venado clay, Ca-bentonite, and Silica gel, which represented different adsorbing surfaces commonly found in soils. Both aqueous and hexane solutions were employed. The solution concentration range of these studies was limited to very low concentrations. The isotherms were obtained for several temperatures in the range 10° to 40°C. A definite degree of decomposition of lindane in the Venado clay-hexane system was observed, so the isotherms for this system were not meaningful. Decomposition of γ-BHC in this system was observed to increase with increasing equilibrium concentration and with increasing temperature. The possibility of β-BHC decomposition in the silica gel-water system was pointed out.

Both normal isotherms (x/m vs. c) and 'corrected' isotherms (x/m vs. c/c_o) were obtained for each system. (c_o refers to the solubility of the isomer in the particular solvent at the given temperature.) The isotherms appeared to be nearly linear, particularly for the aqueous γ-BHC systems. With the exception of the β-BHC-bentonite-water system the normal isotherms were displaced downward with increasing temperature. But the corrected isotherms were displaced upward as temperature increased with the exception of three systems in which the isotherms for 20° and 30°C were nearly superimposed. Comparison of the normal and corrected isotherms led to the conclusion that for these systems the effect of temperature upon solubility is the only factor which in general makes the net adsorptive process exothermic. The normal isotherms for the γ-BHC-Staten peaty muck-hexane system at 10° and 20°C intersected at one point, while the corresponding corrected isotherms diverged throughout the concentration range. The relative adsorbability of aqueous β-BHC on the four adsorbents was seen to be the same as for aqueous γ-BHC with the exception that the positions of silica gel and Ca-bentonite were reversed.

None of the isotherms obeyed a Langmuir plot. But linear log-log plots were obtained for the aqueous γ-BHC and β-BHC systems and for the lower concentration range of the γ-BHC-Staten peaty muck-hexane system. The Freundlich constants k and 1/n were calculated, as well as k', which is comparable to k when $\log(x/m)$ is plotted versus $\log(c/c_o)$. The constants 1/n for each system were observed to increase with temperature according to the theory for dilute solutions. Given this fact it is inevitable that the normal isotherms for a given system will cross, but corrected isotherms will diverge throughout, as long as 1/n remains constant over the entire concentration range.

The constants k and k' are considered useful indices of adsorption. While k values represent hypothetical x/m values at a constant equilibrium concentration, k' values may be considered to represent hypothetical x/m values at nearly constant solution fugacities. With the exception of the silica gel-water systems, higher k values were obtained for aqueous β-BHC adsorption than for γ-BHC. k' values were always lower for β-BHC adsorption from water than for γ-BHC adsorption. The higher k values were, thus, considered to be completely due to the lower solubility of β-BHC in water. When the solubility effect is removed, the adsorbability of γ-BHC is seen to be greater, quite possibly because it, unlike β-BHC, possesses a dipole moment. Higher k' values were obtained for the adsorption of γ-BHC on Staten peaty muck from hexane than from water. One may conclude that at constant solution fugacities lindane competes somewhat more effectively on this soil with hexane than with water. In the case of the hexane solutions adsorption of lindane probably occurs on the inorganic fraction while in aqueous solutions it would probably be adsorbed on the organic fraction.

Equilibrium surface coverages (θ) were low in all the isotherm studies. The maximum value for θ achieved in aqueous systems at 20°C was 1×10^{-4}.

Values for $\Delta \bar{G}^o$ for each isotherm were determined from the initial point values of c_2^s/c_2, because extrapolations to zero concentration yielded unreasonable results. Little change in $\Delta \bar{G}^o$ with temperature was observed. The values of $\Delta \bar{G}^o$ exhibited the same order with respect to the different systems as did the Freundlich k values. $\Delta \bar{H}^o$ and, therefore, $\Delta \bar{S}^o$ values were determined by the Van't Hoff equation. Values of $\Delta \bar{H}^o$ were observed to increase significantly with the γ-BHC-aqueous systems containing Venado clay and Staten peaty muck, indicating a doubtful validity of the use of the integrated Van't Hoff equation. Values for $\Delta \bar{H}^o$ were all negative with the exception of the β-BHC-bentonite-water system. $\Delta \bar{H}^o$ values ranged from + .7 kcal/mole to -8.4 kcal/mole.

'Corrected' values for $\Delta \bar{H}^o$ and $\Delta \bar{S}^o$, designated as $\Delta \bar{H}^{o'}$ and $\Delta \bar{S}^{o'}$, were obtained by substituting $\ln \frac{(Kc_o)_{T_2}}{(Kc_o)_{T_1}}$ for $\ln \frac{K_{T_2}}{K_{T_1}}$ in the Van't Hoff equation. Then, assuming Henry's law behavior for the solute in solution, it was shown that $\Delta \bar{H}^{o'}$ is approximately equal to the difference between the partial molar enthalpy of the solute at the standard state in the adsorbed phase and the molar enthalpy of the pure solid solute. An analogous definition holds in an approximate manner for $\Delta \bar{S}^{o'}$. Values of $\Delta \bar{H}^{o'}$ were positive with three exceptions. Positive $\Delta \bar{H}^{o'}$ values indicated weaker forces operating on the BHC molecules in the adsorbed phase (at standard state) compared to that in the pure solid state. The values of $\Delta \bar{H}^{o'}$ ranged from + 1.1 to 5.8 kcal/mole. All of the $\Delta \bar{S}^{o'}$ values were positive, indicating understandably more degrees of freedom for the BHC molecules in the adsorbed state than in the solid state. The lowest $\Delta \bar{S}^{o'}$ values were obtained for aqueous β-BHC and γ-BHC adsorption on silica gel. This leads to the conclusion that considerable restriction of the freedom of the adsorbed molecules on this adsorbent occurred. Configurational entropy of the adsorbed molecules on this adsorbent could well have been very low. The highest values for $\Delta \bar{S}^{o'}$ were found with aqueous γ-BHC adsorption on Staten peaty muck, Venado clay, and bentonite. Considerable freedom for the molecules adsorbed on these adsorbents is indicated, with the possibility of two-dimensional translational freedom. A lower $\Delta \bar{S}^{o'}$ value was obtained for γ-BHC on Staten peaty muck when adsorbed from hexane than when adsorbed from water. The possibility of water molecules being more mobile on this adsorbent than hexane and so permitting greater freedom for the adsorbed γ-BHC molecules was suggested.

The activity coefficients of the BHC molecules in the adsorbed phase (γ_2^s) were estimated. In aqueous solutions adsorption on Staten peaty muck appeared more ideal (γ_2^s closer to unity) than on Venado clay. Association of adsorbed BHC molecules may occur to some extent on Venado clay while possibly not on the Staten soil.

Isosteric heats (Q_Γ) and heats obtained for a constant change of interfacial tension ($\Delta\sigma$) were calculated. Unlike the isosteric heats, the latter heats, designated as $\Delta \bar{H}_\sigma$, were shown to represent the true difference at equilibrium between the partial molar enthalpy of the adsorbed solute and that of the solute in solution. Values of $\Delta \bar{H}_\sigma$ were calculated from the equation

$$\Delta \bar{H}_\sigma = \frac{R\ T_1 T_2}{T_2 - T_1} \ln \left[\frac{(m_2{}^s/m_2)_{T_2}}{(m_2{}^s/m_2)_{T_1}} \right],$$

where m_2 and $m_2{}^s$ refer to the total mass of solute in solution and in the adsorbed phase at equilibrium, respectively. This equation was derived for dilute solutions assuming Henry's law holds for the solute both in solution and in the adsorbed phase. Calculated Q_Γ values were observed to be of the same order of magnitude for each isotherm as the $\Delta \bar{H}_\sigma$ values, but the trend of Q_Γ with changing surface coverage was observed to differ in some cases from that of the $\Delta \bar{H}_\sigma$ values.

The decrease of $\Delta \bar{H}_\sigma$ with surface coverage was shown in γ-BHC systems to be clear and definite in the case of adsorption on bentonite and silica gel from water, and on Staten peaty muck from hexane. But a very gradual $\Delta \bar{H}_\sigma$ decrease was observed for γ-BHC adsorption in the Staten peaty muck-water and Venado clay-water systems. This led to the conclusion that in the surface coverage range studied there is a definite site energy range on inorganic surfaces, but a relatively small range of site energies on the organic fractions of the adsorbents. Values for $\Delta \bar{S}_{\sigma}$ were calculated from the fact that $\Delta \bar{H}_{\sigma} = T \Delta \bar{S}_{\sigma}$ at any point on the isotherm.

Values for $\Delta \bar{H}'$ were calculated in a manner analogous to that for obtaining $\Delta \bar{H}^{o'}$, but employing as the basic equation the one presented above for $\Delta \bar{H}_{\sigma}$. $\Delta \bar{H}'$ is defined as $\Delta \bar{H}' = \bar{H}_2^s - \bar{H}_s$, where $\bar{H}_2^s$ is the partial molar heat content of the solute adsorbed on the adsorbent at equilibrium and $\bar{H}_s$ is the molar enthalpy of the solid solute. Assuming that a higher molar enthalpy holds for solid β-BHC than for solid γ-BHC a graphical representation was presented to explain differences in $\Delta \bar{H}'$ values between aqueous β-BHC and aqueous γ-BHC systems. Values of $\Delta \bar{S}'$ were observed to increase uniformly with increasing surface coverage. Assuming a range of site energies, it is to be expected that as coverage increases the average number of degrees of freedom of the adsorbed molecules will increase. In contrast, the $\Delta \bar{S}_{\sigma}$ values were negative, with the exception of the β-BHC-bentonite-water system. More freedom for the solute molecules would be expected in solution than in the adsorbed state. It is likely that the configurational entropy of β-BHC adsorbed from water on bentonite is quite high. As observed for the $\Delta \bar{S}^{o'}$ values, lowest $\Delta \bar{S}'$ values were obtained for γ-BHC and β-BHC adsorption from water on silica gel.

Integral values for the free energy of adsorption (ΔG) were calculated for each system. Maximum ΔG values obtained at 20°C ranged from -1.2×10^{-5} to -132×10^{-5} calories for the systems studied. ΔG^B, the change in free energy due to dilution of the bulk solution accompanying adsorption, constituted a greater contribution to ΔG than did ΔG^a, the decrease in surface free energy.

Values for the integral heats of adsorption were determined for two systems. Essentially linear plots of ΔH versus x/m were obtained. Values for $-\Delta H$ in the two systems were seen to increase with temperature.

PRACTICAL IMPLICATIONS

The systems studied in this investigation are rather complex from a chemical point of view. Yet, they appear relatively simple compared to the phenomena occurring at the time of the application of an insecticide to agricultural soils and during subsequent leaching of the soil. It is, consequently, somewhat precarious to extrapolate the findings from such a laboratory study to field conditions. Nevertheless, if one recognizes the tentative nature of such proposed applications, the conclusions may prove to be of some practical value to the farmer or legislator.

The immediate fate of an amount of lindane applied directly to, or indirectly reaching, the surface of the soil should depend to some extent upon the manner of formulation. One would expect, for example, much lower volatilization losses for lindane applied on dust diluents than in the form of an emulsion or dissolved in some organic solvent.

So as to impart some kind of quantitative understanding of a few of the factors involved, we shall limit our discussion to a particular set of field conditions. Let us assume that lindane, applied in an emulsified form at a normal rate of 10 lb/acre, has come in contact with a field soil which is dry or only very slightly moist. We shall assume that all the lindane so applied reaches the soil surface and penetrates only the top one-tenth inch of the surface. Then, let us further assume that the field is not irrigated for 30 days and that rain does not fall in that period. It is likely that the polar end of the molecules of the emulsifying agent would become adsorbed on the soil to some extent, and, thus, the globules of organic solvent carrying the lindane would tend to be drawn to the soil surface. Within a few hours following application some adsorption of lindane on the soil would be expected. We will assume that the soil is slightly acid in reaction and that the properties of the organic solvent or the emulsifier employed would not tend to favor decomposition of lindane. During the process of evaporation of the water and solvent of the emulsion at the soil surface some lindane would be volatilized.

The writer conducted an experiment to determine the rate of volatilization of lindane applied in benzene solutions to a thin soil layer. (This is described in the Appendix. See Table A-8.) After 30 days about 9% of the applied lindane remained on the soil (Venado clay). Assuming that this rate of volatilization holds for the 10 lb/acre application on our hypothetical field of lindane in an emulsified form (equivalent to 1.75 times the experimental rate), there would remain about 32 µg of lindane for each gram of soil in the top one-tenth inch of the surface.

With the advent of rains, or irrigation, following the 30-day period the problem becomes one of aqueous desorption of the lindane from the surface by leaching. This is a very complex process. We will attempt, however, to estimate by means of the aqueous γ-BHC isotherm for 20°C the volume of water required to reduce by leaching the given amount of lindane (32 µg/gm of soil) to a relatively low level (1.0 µg/gm) in the top one-tenth inch layer. We may consider the leaching process in a soil to occur in small increments involving the successive transfer of water in the pores. Assuming no hysteresis, desorption will follow the adsorption isotherm. Each increment of water percolating below will contain a somewhat lower concentration of lindane than the one preceding it. As a first approximation one can consider, then, that the total volume of water (V) needed to leach away 31 of the 32 μg from each gram of the surface layer can be found from

$$V = \frac{(x/m)_{max} - (x/m)_{min}}{c_{av}} \qquad (64)$$

where $(x/m)_{max}$ is the amount adsorbed per gram in equilibrium with the first increment of aqueous solution, $(x/m)_{min}$ is the desired lowest level of adsorption chosen (in this case 1.0 μg/gm), and c_{av} is the average of the two concentrations which are in equilibrium with $(x/m)_{max}$ and $(x/m)_{min}$, respectively. If one assumes a porosity of 50% and a bulk density of 1.3 for a soil, the volume of each increment of water which comes into equilibrium with a gram of soil is 0.77 ml. Table 39 shows the estimated volumes of water required to leach the top surface in the manner described.

Table 39

Estimation of the Volume of Water Required to Leach the Top One-Tenth Inch layer of Soil at 20°C

(Initial lindane concentration on soil = 32 μg/gm;
Final lindane concentration on soil (top layer) = 1.0 μg/gm)

	Staten peaty muck	Venado clay	Silica gel
$(x/m)_{max}$ (μg/gm)	32	31.4	26.6
c at $(x/m)_{max}$ (μg/ml)	0.096	0.80	7.0 (saturated)
c at x/m = 1	0.0025	0.0125	0.125
c_{av} (μg/ml)	0.049	0.406	3.56
V (ml H_2O/gm)	630	75	7.2
V (inches of H_2O)	81	9.7	0.93

Table 39 indicates that about 87 times more water is required to leach Staten peaty muck than a soil with adsorptive properties like silica gel (such as Oakley sand). Ten times more water is required to leach lindane from the top layer of Venado clay than a sand.

It is important to note that the volumes of water required for leaching (shown in Table 39) are based on equilibrium considerations. But equilibrium is frequently not achieved between the adsorbing surface and percolating waters because of time considerations. Thus, these values underestimate the actual volumes of water needed for leaching in all cases except that involving extremely slow, and perhaps intermittent, leaching. Because of the higher degree of capillary porosity with Venado clay and its consequent low hydraulic conductivity, the difference between the estimated volume and the actual volume of water required for leaching should be proportionately less than that for the other two types of soil. The relatively high hydraulic conductivity of a sand indicates that the value of 0.93" would be definitely low for such 'open' soils in the field.

Recognizing the volumes given in Table 39 are underestimates, we may, nevertheless, discuss their significance with respect to the possibility of the accumulation of lindane. It can be seen that for most cultivated areas under normal rainfall and irrigation management it would require two or three years to leach the lindane from Staten peaty muck to the specified extent. But soils similar to Venado clay or silica gel could usually be leached in a single season. Accumulation in this surface layer would appear to be a serious possibility only in the case of organic soils, such as Staten peaty muck.

The progressive advance of lindane through the profile leached from the top layer should be slow, involving continual and repeated adsorption and desorption. One would expect a time series of concentration vs. depth curves gradually descending -- similar to the distribution of a salt in a soil with time following a single application. These chromatographic or aqueous leaching characteristics of lindane in soils would be fruitfully explored directly by means of laboratory column studies.

APPENDIX

Table A-1

Values of c and x/m (L. S. analysis)
(in μg/ml and μg/gm, respectively)

Isomer and Solvent	Temp. (°C)	Ca-Staten peaty muck			Ca-Venado clay		
		x/m	c	$\frac{c}{x/m}$	x/m	c	$\frac{c}{x/m}$
γ-BHC in water	10	.274	.000534	.001946	.265	.00226	.008512
		2.45	.004866	.001986	2.35	.02529	.01076
		4.90	.01057	.002157	4.66	.05784	.01241
		9.79	.02261	.002309	9.25	.12998	.01405
		24.5	.05770	.002355	22.8	.3906	.01713
	20	.273	.000662	.00242	.265	.002269	.00855
		2.44	.006297	.00258	2.33	.02772	.01189
		4.88	.01259	.00258	4.62	.06508	.01409
		9.75	.02608	.00267	9.17	.14360	.01566
		24.38	.06906	.00283	22.46	.45206	.02013
	30	.271	.000894	.00330	.263	.002583	.009814
		2.43	.008004	.00329	2.31	.03169	.01372
		4.85	.01672	.00345	4.57	.07358	.01610
		9.70	.03386	.00349	9.04	.16394	.01813
		24.23	.08708	.00359	22.20	.49340	.02222
	40	.269	.001218	.004523	.260	.003011	.01159
		2.40	.01173	.00489	2.27	.03701	.01631
		4.81	.02234	.00464	4.49	.08530	.01900
		9.61	.04456	.00464	8.91	.18344	.02059
		23.98	.12107	.00505	21.71	.57440	.02646
γ-BHC in hexane	10	.102	.08124	.7965			
		.473	.4140	.8754			
		.851	.8472	.9956			
		2.18	2.6119	1.1981			
		6.76	8.823	1.3052			
		20.99	46.674	2.224			
		62.40	190.85	3.058			
		161.30	476.46	2.954			
	20	.0826	.08388	1.0154			
		.358	.4305	1.2026			
		.712	.8619	1.2105			
		2.11	2.5866	1.2259			
		6.17	8.8102	1.4279			
		22.2	45.772	2.0618			
		79.0	184.92	2.3408			
		157.0	470.71	2.9982			
β-BHC in water	20	.37	.000549	.00148	0.36	.00252	.00700
		.95	.00155	.00163	0.92	.00722	.00785
		1.80	.00288	.00160	1.73	.01509	.00872
		2.11	.00348	.00165	2.03	.01911	.00941
		2.28	.00445	.00195	2.18	.02424	.01112
	30	.366	.000792	.00216	.354	.00311	.00878
		.945	.00196	.00207	.911	.00800	.00878
		1.79	.00379	.00212	1.72	.0180	.01046
		2.10	.00470	.00224	2.01	.0220	.01094
		2.27	.00524	.00231	2.17	.0251	.01157

Table A-1 (cont.)

Values of c and x/m (L. S. analysis)
(in µg/ml and µg/gm, respectively)

Isomer and Solvent	Temp. (°C)	Ca-Bentonite			Silica Gel		
		x/m	c	$\frac{c}{x/m}$	x/m	c	$\frac{c}{x/m}$
γ-BHC in water	20	.128	.02985	.2338	.175	.02044	.1170
		1.01	.2926	.2897	1.51	.1928	.1276
		1.87	.6156	.3292	2.94	.4010	.1364
		3.68	1.2418	.3374	5.79	.8194	.1415
		8.18	3.3080	.4044	13.83	2.1770	.1574
γ-BHC in water	30	.116	.03205	.2765	.142	.02680	.1884
		.927	.3076	.3319	1.22	.2487	.2038
		1.80	.6280	.3489	2.45	.4966	.2027
		3.52	1.2692	.3606	4.75	1.0224	.2152
		7.81	3.3706	.4316	11.40	2.6524	.2327
β-BHC in water	19.8	.206	.0328	.1592	.118	.0504	.4271
		.502	.0905	.1803	.294	.1321	.4493
		.911	.1797	.1972	.553	.2513	.4544
		1.04	.2165	.2082	.659	.2931	.4448
		1.10	.2415	.2195	.703	.3204	.4558
β-BHC in water	30	.210	.0320	.1524	.094	.0553	.5883
		.520	.0871	.1675	.245	.142	.5796
		.940	.173	.1840	.455	.270	.5934
		1.10	.204	.1854	.525	.319	.6076
		1.08	.244	.2259	.535	.353	.6598

Table A-2

Isotherm Studies

Comparison of Equilibrium Concentration Values by Liquid Scintillation Counting and Gas Chromatography (in µg/ml)

Adsorbate, Solvent, and Temp.	Standard soln. conc.	Ca-Staten Peaty Muck		Ca-Venado Clay		Ca-Bentonite		Silica Gel	
		L.S.	G.C.	L.S.	G.C.	L.S.	G.C.	L.S.	G.C.
γ-BHC	0.10	.000534	.000612	.00226	.00233				
in	0.50	.00487	.00760	.0253	.0400				
water	1.0	.0106	.0153	.0578	.0854				
at 10°C	2.0	.0226	.0290	.1300	.182				
	5.0	.0577	.0650	.391	.485				
γ-BHC	0.10	.000662	.000871	.00227	.00357	.0298	.0310	.0204	.0218
in	0.50	.00630	.00795	.0277	.0355	.293	.291	.193	.182
water	1.0	.0126	.0152	.0651	.0781	.616	.606	.401	.393
at 20°C	2.0	.0261	.0291	.144	.176	1.24	1.22	.819	.762
	5.0	.0691	.0660	.452	.497	3.31	3.26	2.18	2.09
γ-BHC	0.10	.000894	.00107	.00258	.00301	.0320	.0316	.0268	.0264
in	0.50	.00800	.00963	.0317	.0323	.308	.308	.249	.238
water	1.0	.0167	.0169	.0736	.0755	.628	.666	.497	.514
at 30°C	2.0	.0339	.0355	.164	.175	1.27	1.31	1.02	1.03
	5.0	.0871	.0800	.493	.505	3.37	3.39	2.65	2.69
γ-BHC	0.10	.00122	.00183	.00301	.00472				
in	0.50	.0117	.0153	.0370	.0446				
water	1.0	.0223	.0250	.0853	.0998				
at 40°C	2.0	.0446	.0436	.183	.217				
	5.0	.121	.0911	.574	.535				
β-BHC	.074	.000549	+	.00252	+	.0328		.0504	
in	.191	.00155	+	.00722	+	.0905		.132	.123
water	.361	.00288	+	.0151	+	.180	.177	.251	.218
at 20°C*	.424	.00348	+	.0191	+	.216	.194	.293	.248
	.460	.00445	.0025	.0242	.018	.241	.218	.320	.269

Table A-2 (cont.)

Isotherm Studies

Comparison of Equilibrium Concentration Values by Liquid Scintillation Counting and Gas Chromatography (in μg/ml)

Adsorbate, Solvent, and Temp.	Standard Solution	Ca-Staten Peaty Muck		Ca-Venado Clay		Ca-Bentonite		Silica Gel	
		L.S.	G.C.	L.S.	G.C.	L.S.	G.C.	L.S.	G.C.
β-BHC	.074	.000792	+	.00311	+	.0320		.0553	
in	.191	.00196	+	.00800	+	.0871		.142	
water	.361	.00379	+	.0180	+	.173	.189	.270	.245
at 30°C	.424	.00470	+	.0220	+	.204	.214	.319	.281
	.460	.00524	+	.0251	.026	.244		.353	
γ-BHC	.10	.0812	.0835	.0415	.0000				
in	.50	.414	.436	.406	.154				
nanograde	1.0	.847	.846	.485	.0525				
hexane	3.0	2.61	2.78	1.73	.687				
at 10°C	10.0	8.82	9.05	5.92	3.47				
	50.0	46.67	46.71	35.27	26.91				
	200.0	190.8	192.4	76.37	67.04				
	500.0	476.5	455.0	206.4	183.8				
	.10	.0839	.0902	.0415	.00000				
γ-BHC	.50	.430	.442	.211	.000018				
in	1.0	.862	.850	.431	.000367				
nanograde	3.0	2.59	2.63	1.43	.0766				
hexane	10.0	8.81	9.07	3.87	.964				
at 20°C	50.0	45.77	46.27	18.86	10.84				
	200.0	184.9	195.1	78.54	61.77				
	500.0	470.7	465.1	220.3	172.6				

Table A-2 (cont.)

Isotherm Studies

Comparison of Equilibrium Concentration Values by Liquid Scintillation Counting and Gas Chromatography (in µg/ml)

Adsorbate, Solvent, and Temp.	Standard Solution	Ca-Staten Peaty Muck		Ca-Venado Clay		Ca-Bentonite		Silica Gel	
		L.S.	G.C.	L.S.	G.C.	L.S.	G.C.	L.S.	G.C.
	.10			.0425	.000234				
γ-BHC	.50			.222	.000267				
in	1.0			.426	.000212				
nanograde	3.0			1.33	.0129				
hexane	10.0			4.09	.557				
at 30°C	50.0			21.02	10.81				
	200.0			85.98	59.17				
	500.0			222.3	182.7				

Underlined values indicate instances in which L.S. values exceed G.C. values.

+ Indicates concentration too low to analyze by gas chromatography.

* For the Silica gel and Ca-bentonite determinations the bath temperature was only 19.8°C.

Table A-3

Tabulation of Reduced Concentration for Isotherm Studies

	Ca-Staten Peaty Muck			Ca-Venado Clay			Ca-Bentonite			Silica Gel		
	x/m	c	c/co*	x/m	c	c/co	x/m	c	c/co	x/m	c	c/co
γ-BHC	.273	.000662	.0000777	.265	.002269	.000266	.128	.02985	.003503	.1747	.02044	.002399
at	2.44	.006297	.000739	2.33	.02772	.003253	1.01	.2926	.03434	1.51	.1928	.02263
20°C in	4.88	.01259	.001478	4.62	.06508	.007638	1.87	.6156	.07225	2.94	.4010	.04706
H_2O	9.75	.02608	.003061	9.17	.14360	.01685	3.68	1.2418	.14575	5.79	.8194	.09617
(L.S.)	24.38	.06906	.008105	22.46	.45206	.05306	8.18	3.3080	.3883	13.83	2.1770	.2555
γ-BHC	.271	.000894	.0000680	.263	.002583	.000196	.1159	.03205	.002439	.1422	.02680	.002040
at	2.43	.008004	.000609	2.31	.03169	.002412	.927	.3076	.02341	1.22	.2487	.01893
30°C in	4.85	.01672	.001272	4.57	.07358	.005600	1.80	.6280	.04779	2.45	.4966	.03779
H_2O	9.70	.03386	.002577	9.04	.16394	.01248	3.52	1.2692	.09659	4.75	1.0224	.07781
(L.S.)	24.23	.08708	.006627	22.20	.49340	.03755	7.81	3.3706	.2565	11.40	2.6524	.20186
			x 10-5									
	.102	.08124	.8327									
γ-BHC	.473	.4140	4.244									
at	.851	.8472	8.684									
10°C in	2.18	2.6119	26.772									
nanograde	6.76	8.823	90.436									
hexane	20.99	46.674	478.41									
(L.S.)	62.40	190.847	1,956.2									
	161.30	476.461	4,883.7									
			x 10-5									
	.0826	.08388	.6002									
γ-BHC	.358	.4305	3.081									
at	.712	.8619	6.168									
20°C in	2.11	2.5866	18.510									
nanograde	6.17	8.8102	63.046									
hexane	22.2	45.772	327.54									
(L.S.)	79.0	184.92	1,323.3									
	157.0	470.71	3,368.4									

Table A-3 (cont.)

Tabulation of Reduced Concentration for Isotherm Studies

	Ca-Staten Peaty Muck			Ca-Venado Clay			Ca-Bentonite			Silica Gel		
	x/m	c	c/c_o*	x/m	c	c/c_o	x/m	c	c/c_o	x/m	c	c/c_o
β-BHC at	.37	.000549	.000203	.36	.00252	.000933	.206	.0328	.01215	.118	.0504	.01867
20°C	0.95	.00155	.000574	.92	.00722	.002674	.502	.0905	.03352	.294	.1321	.04893
(19.8)	1.80	.00288	.001067	1.73	.01509	.005589	.911	.1797	.06656	.553	.2513	.09307
in H_2O	2.11	.00348	.001289	2.03	.01911	.007078	1.04	.2165	.08018	.659	.2931	.10856
(L.S.)	2.28	.00445	.001648	2.18	.02424	.008978	1.10	.2415	.08944	.703	.3204	.11867
β-BHC at	.366	.000792	.000219	.354	.00311	.000861	.210	.0320	.008864	.094	.0553	.01532
30°C in	.945	.00196	.000543	.911	.00800	.002216	.520	.0871	.02413	.245	.142	.03934
H_2O	1.79	.00379	.001050	1.72	.0180	.004986	.940	.173	.04792	.455	.270	.07479
(L.S.)	2.10	.00470	.001302	2.01	.0220	.006094	1.10	.204	.05651	.525	.319	.08836
	2.27	.00524	.001452	2.17	.0251	.006953	1.08	.244	.06759	.535	.353	.09778

* c_o = solubility in given solvent at given temperature.

Calculation of c_2^s

x/m = µg solute adsorbed per gram of adsorbent.

c_2 = µg of solute per ml of solution at equilibrium.

For dilute solutions $c_2 \cong$ µg of solute per ml of solvent at equilibrium.

We define c_2^s = µg of solute adsorbed per ml of solvent in contact with adsorbent surface at equilibrium.

Then,

$$c_2^s = (n^s/n)(\rho_1/M_1), \tag{1}$$

where n^s is the number of µg of solute adsorbed per cm^2 of surface, n is the number of moles of solvent on the adsorbent per cm^2 of surface, ρ_1 is the density of the solvent, and M_1 is the molecular weight of the solvent. ρ_1/M_1 is the number of moles of solvent per ml pure solvent.

Now,

$$n^s = \frac{x/m}{s}, \tag{2}$$

where s is the surface area of the adsorbent in cm^2 per gram.

In addition,

$$\theta = \frac{n^s\ N\ A_2}{M_2 \times 10^6}, \tag{3}$$

where θ is the fraction of the adsorbent surface area covered by solute molecules, N is Avogadro's number, A_2 is the cross-sectional area of the solute molecule in cm^2, and M_2 is the molecular weight of the solute. Then, assuming the surface to be completely covered, it follows that

$$n = \frac{1 - \theta}{A_1\ N}, \tag{4}$$

where A_1 is the cross-sectional area of the solvent molecule in cm^2. Combining equations (1), (2), (3), and (4), we arrive at an expression for c_2^s which is useful in terms of experimental data.

$$c_2^s = \frac{(\rho_1/M_1)\,A_1}{\frac{s}{N(x/m)} - \frac{A_2}{M_2 \times 10^6}}\,.$$

For the BHC molecule the term $A_2/(M_2 \times 10^6)$ equals 1.496×10^{-23}. But it turns out that this term is so small compared with $s/N(x/m)$ that it may be neglected. In the following table (Table A-4) c_2^s is given in terms of x/m for each solvent-adsorbent system in the isotherm studies.

Calculation of c_2^s

Table A-4

	Solvent	Ca-Staten peaty muck	Ca-Venado clay	Ca-bentonite	Silica gel
s_2 (cm^2)		2.33×10^6	4.22×10^6	8.10×10^6	8.9×10^6
s/N		3.87×10^{-18}	7.01×10^{-18}	1.34×10^{-17}	1.48×10^{-17}
$(\rho_1/M_1)A_1$	water	5.88×10^{-17}	5.88×10^{-7}	5.88×10^{-17}	5.88×10^{-17}
c_2^s (μg/ml)	water	15.212 (x/m)	8.399 (x/m)	4.376 (x/m)	3.970 (x/m)
$(\rho_1/M_1)A_1$	hexane	3.58×10^{-17}	3.58×10^{-17}	3.58×10^{-17}	3.58×10^{-17}
c_2^s (μg/ml)	hexane	9.261 (x/m)	5.113 (x/m)	-	-

Table A-5

Determination of $\Delta \bar{G}^o$, $\Delta \bar{H}^o$, and $\Delta \bar{S}^o$ by the Method of Extrapolating to Zero x/m

System	T °C	log K_o	$\Delta \bar{G}^o$	$\Delta \bar{H}^o$	Av. $\Delta \bar{G}^o$	$\Delta \bar{S}^o$
γ-BHC-Ca-Staten Peaty Muck-water	10	3.8932	-5,044			
				-3,260	-5,080	+6.31
	20	3.8074	-5,110			
				-4,980	-5,110	+0.443
	30	3.6850	-5,110			
				-6,820	-5,080	-5.62
	40	3.5281	-5,060			
γ-BHC Ca-Venado Clay-water	10	3.0448	-3,940			
				+2,690	-4,060	+23.44
	20	3.1157	-4,180			
				-862	-4,236	+11.31
	30	3.0945	-4,290			
				-1,255	-4,343	+10.02
	40	3.0656	-4,390			
γ-BHC-Ca-Bentonite-water	20	1.3152	-1,760			
				+109,100	-3,650	+378.1
	30	3.9977	-5,540			
γ-BHC-Silica Gel-water	20	1.5407	-2,070			
				-586	-2,090	+5.05
	30	1.5263	-2,120			
γ-BHC-Ca-Staten Peaty Muck-hexane	10	1.0708	-1,390			
				+52,060	-2,330	+188.8
	20	2.4415	-3,280			
β-BHC-Ca-Staten Peaty Muck-water	20	4.0131	-5,380			
				-5,980	-5,370	-2.03
	30	3.8661	-5,360			
β-BHC-Ca-Venado Clay-water	20	3.1887	-4,280			
				-8,010	-4,210	-12.72
	30	2.9918	-4,150			
β-BHC-Ca-Bentonite-water	19.8	1.8951	-2,540			
				-15,010	-2,320	-42.57
	30	1.5183	-2,110			
β-BHC-Silica Gel-water	19.8	4.1592	-5,580			
				-132,400	-3,370	-432.9
	30	0.8360	-1,160			

Table A-6

Surface Activity Coefficients (γ_2^s)

System	T (°C)	c_2/c_2^s	K_o (from initial point)	γ_2^s	x/m
γ-BHC-Ca-Venado clay-water	10	.001014	986.2	1.000	.265
		.001281		1.263	2.35
		.001478		1.458	4.66
		.001673		1.650	9.25
		.002040		2.012	22.8
	20	.001018	982.3	1.000	.265
		.001416		1.391	2.33
		.001678		1.648	4.62
		.001865		1.832	9.17
		.002397		2.355	22.46
	30	.001168	856.2	1.000	.263
		.001634		1.399	2.31
		.001917		1.641	4.57
		.002159		1.848	9.04
		.002646		2.265	22.20
	40	.001380	724.6	1.000	.260
		.001942		1.407	2.27
		.002262		1.639	4.49
		.002451		1.776	8.91
		.003150		2.283	21.71
γ-BHC-Ca-Staten peaty muck-water	10	.0001279	7,819	1.000	.274
		.0001306		1.021	2.45
		.0001418		1.109	4.90
		.0001518		1.187	9.79
		.0001548		1.210	24.5
	20	.0001591	6,285	1.000	.273
		.0001696		1.066	2.44
		.0001696		1.066	4.88
		.0001755		1.103	9.75
		.0001860		1.169	24.38
	30	.0002169	4,610	1.000	.271
		.0002163		0.997	2.43
		.0002268		1.046	4.85
		.0002294		1.058	9.70
		.0002360		1.088	24.23
	40	.0002973	3,364	1.000	.269
		.0003213		1.081	2.40
		.0003053		1.027	4.81
		.0003048		1.025	9.61
		.0003318		1.116	23.98

Table A-6 (cont.)

Surface Activity Coefficients (γ_2^s)

System	T (°C)	c_2/c_2^s	K_o (from initial point)	γ_2^s	x/m
γ-BHC-Silica gel-water	20	.02947	33.93	1.000	.175
		.03214		1.090	1.51
		.03436		1.166	2.94
		.03565		1.210	5.79
		.03965		1.345	13.83
	30	.04746	21.07	1.000	.142
		.05134		1.082	1.22
		.05106		1.076	2.45
		.05421		1.142	4.75
		.05862		1.235	11.40
γ-BHC-Ca-bentonite-water	20	.05343	18.72	1.000	.128
		.06620		1.239	1.01
		.07523		1.408	1.87
		.07711		1.443	3.68
		.09242		1.730	8.18
	30	.06319	15.82	1.000	.116
		.07585		1.200	.927
		.07973		1.261	1.80
		.08241		1.304	3.52
		.09863		1.560	7.81
γ-BHC-Ca-Staten peaty muck-hexane	10	.08601	11.63	1.000	.102
		.09452		1.099	.473
		.10750		1.250	.851
		.12937		1.504	2.18
		.14094		1.639	6.76
		.24015		2.792	20.99
		.33025		3.840	62.40
		.31897		3.709	161.3
	20	.10964	9.121	1.000	.083
		.12986		1.184	.358
		.13071		1.192	.712
		.13237		1.207	2.11
		.15418		1.406	6.17
		.22263		2.031	22.2
		.25276		2.305	79.0
		.32375		2.953	157.0

Table A-6 (cont.)

Surface Activity Coefficients (γ_2^s)

System	T (^{o}C)	c_2/c_2^s	K_o (from initial point)	γ_2^s	x/m
β-BHC-Ca-Venado clay-water	20	.0008335	1,200	1.000	.36
		.0009347		1.121	.92
		.001038		1.245	1.73
		.001120		1.344	2.03
		.001324		1.588	2.18
	30	.001045	956.9	1.000	.354
		.001045		1.000	.911
		.001245		1.191	1.72
		.001303		1.247	2.01
		.001378		1.319	2.17
β-BHC-Ca-Staten peaty muck-water	20	.0000973	10,280	1.000	.37
		.0001072		1.102	.95
		.0001052		1.081	1.80
		.0001085		1.115	2.11
		.0001282		1.318	2.28
	30	.0001420	7,042	1.000	.366
		.0001361		0.958	.945
		.0001394		0.982	1.79
		.0001472		1.037	2.10
		.0001518		1.069	2.27
β-BHC-Silica gel-water	19.8	.10760	9.29	1.000	.118
		.11319		1.052	.294
		.11447		1.064	.553
		.11205		1.041	.659
		.11482		1.067	.703
	30	.14820	6.75	1.000	.094
		.14601		0.985	.245
		.14949		1.009	.455
		.15307		1.033	.525
		.16622		1.122	.535
β-BHC-Ca-bentonite-water	19.8	.03638	27.49	1.000	.206
		.04120		1.132	.502
		.04507		1.239	.911
		.04758		1.308	1.04
		.05016		1.379	1.10
	30	.03483	28.71	1.000	.210
		.03828		1.099	.520
		.04205		1.207	.940
		.04237		1.216	1.10
		.05162		1.482	1.08

Table A-7

Calculation of Values of $-A_T\Delta\sigma$ and Associated Values of m_2^s/m_2 and $(m_2^s/m_2)m_o$

$(Z = \left[\frac{5 \times 10^{-6}}{M_2}\right] R\ T)$

Ca-Staten peaty muck

Isomer and Solvent	T (°C)	Z	Freundlich k	n	$c^{1/n}$	$-A_T\Delta\sigma \times 10^5$	m_2^s/m_2	$\frac{m_2^s}{m_2/m_o}$
γ-BHC in water	10	9.673×10^{-6}	377	1.046	.000745	.284	105.2	
					.006148	2.34	95.26	
					.01291	4.92	92.09	
					.02669	10.18	89.01	
					.06539	24.94	85.45	
	20	10.0149×10^{-6}	331	1.0322	.000832	.285	83.20	17,722
					.007375	2.52	77.53	16,514
					.01443	4.94	75.87	16,160
					.02920	9.99	74.12	15,787
					.07506	25.68	71.95	15,326
	30	10.3565×10^{-6}	269	1.0198	.001024	.291	61.61	20,239
					.008790	2.50	59.08	19,409
					.01809	5.14	58.21	19,121
					.03616	10.27	57.45	18,874
					.09130	25.94	56.41	18,530
	40	10.6982×10^{-6}	197	1.0174	.001367	.293	44.22	
					.01265	2.71	42.50	
					.02384	5.11	42.05	
					.04700	10.08	41.56	
					.1255	26.91	40.84	

Table A-7 (cont.)

Ca-Staten peaty muck

Isomer and Solvent	T (°C)	Z	Freundlich k	n	$c^{1/n}$	$-A_T\Delta\sigma \times 10^5$	m_2^s/m_2	$\frac{m_2^s}{m_2/m_o}$
β-BHC in water	20	10.0149×10^{-6}	456	1.0531	.000801	.386	133.2	8,993
					.002147	1.03	126.3	8,527
					.003868	1.86	122.5	8,268
					.004629	2.23	121.3	8,188
	30	10.3565×10^{-6}	437	1.0104	.0008524	.390	94.02	8,485
					.002090	.956	93.19	8,411
					.004014	1.84	92.56	8,354
					.004967	2.27	92.37	8,336
γ-BHC in hexane	10	9.6733×10^{-6}	.974	1.1285	.10814	.115	.259	63,274
					.45774	.487	.215	52,560
					.86338	.918	.199	48,440
					2.3413	2.49	.174	42,560
					6.8850	7.32	.152	37,100
	20	10.0149×10^{-6}	.823	1.0696	.09855	.087	.193	67,560
					.45477	.401	.174	60,750
					.87034	.767	.166	58,060
					2.4315	2.14	.155	54,010
					7.6486	6.74	.143	49,920

Table A-7 (cont.)

Ca-Venado clay

Isomer and Solvent	T (°C)	Z	Freundlich k	n	$c^{1/n}$	$-A_T\Delta\sigma$ x 10^5	m_2^s/m_2	$\frac{m_2^s}{m_2/m_o}$
γ-BHC in water	10	9.6733×10^{-6}	53.8	1.1550	.005118	.308	24.36	
					.04143	2.49	17.63	
					.08475	5.09	15.77	
					.1710	10.28	14.16	
					.4431	26.63	12.21	
	20	10.0149×10^{-6}	45.7	1.1888	.005969	.325	24.05	5,122
					.04901	2.666	16.16	3,442
					.1005	5.47	14.11	3,006
					.1955	10.64	12.44	2,650
					.5128	27.90	10.37	2,210
	30	10.3565×10^{-6}	41.3	1.1832	.006496	.329	20.77	6,824
					.05408	2.74	14.10	4,630
					.11025	5.58	12.38	4,066
					.21703	10.98	10.93	3,592
					.55041	27.86	9.21	3,027
	40	10.6982×10^{-6}	36.1	1.1813	.007345	.335	17.62	
					.06135	2.80	11.97	
					.12448	5.68	10.54	
					.23798	10.86	9.37	
					.62540	28.53	7.86	
β-BHC in water	20	10.0149×10^{-6}	62.8	1.1618	.005800	.424	28.91	1,951
					.014349	1.05	24.96	1,685
					.027066	1.98	22.53	1,521
					.033168	2.42	21.80	1,472
	30	10.3565×10^{-6}	60.2	1.1322	.006104	.431	23.63	2,133
					.014061	.992	21.16	1,910
					.028779	2.03	19.25	1,737
					.034357	2.42	18.80	1,697

Table A-7 (cont.)

Ca-bentonite

Isomer and Solvent	T (^oC)	Z	Freundlich k	n	$c^{1/n}$	$-A_T\Delta\sigma$ x 10^5	$m_2{}^s/m_2$	$\frac{m_2{}^s}{m_2/m_o}$
γ-BHC in water	20	10.0149×10^{-6}	2.92	1.1280	.044463	.147	.870	185.2
					.33642	1.11	.671	143.0
					.65046	2.14	.617	131.6
					1.2117	4.00	.570	121.4
					2.8881	9.53	.510	108.6
	30	10.3565×10^{-6}	2.71	1.0978	.043544	.134	.736	241.9
					.34168	1.05	.602	197.8
					.65463	2.02	.565	185.6
					1.2425	3.83	.531	174.3
					3.0247	9.32	.486	159.8
β-BHC in water	19.8	10.0081×10^{-6}	3.96	1.1583	.05233	.240	1.263	85.28
					.12566	.577	1.100	74.24
					.22725	1.04	1.002	67.61
					.26689	1.225	.976	65.90
	30	10.3565×10^{-6}	4.46	1.1299	.04754	.248	1.325	119.6
					.11532	.602	1.181	106.6
					.21165	1.10	1.091	98.5
					.24491	1.28	1.071	96.6

Table A-7 (cont.)

Silica gel

Isomer and Solvent	T (^{o}C)	Z	Freundlich k	n	$c^{1/n}$	$-A\frac{\Delta\sigma}{T} \times 10^5$	m_2^s/m_2	$\frac{m_2^s}{m_2/m_o}$
γ-BHC in water	20	10.0149×10^{-6}	6.88	1.0655	.025966	.191	1.748	372.3
					.21334	1.57	1.523	324.3
					.42414	3.11	1.455	310.0
					.82950	6.090	1.393	296.7
					2.0755	15.24	1.312	279.4
	30	10.3565×10^{-6}	4.62	1.0447	.031281	.156	1.078	354.2
					.26398	1.32	0.981	322.2
					.51169	2.558	0.952	312.8
					1.0214	5.11	0.923	303.2
					2.5437	12.72	0.886	291.1
β-BHC in water	19.8	10.0081×10^{-6}	2.13	1.0294	.054893	.120	0.464	31.31
					.13997	.307	0.451	30.46
					.26143	.574	0.443	29.91
					.30356	.666	0.441	29.78
	30	10.3565×10^{-6}	1.64	1.0152	.057751	.100	0.342	30.91
					.14622	.252	0.338	30.48
					.27538	.475	0.334	30.19
					.32452	.560	0.334	30.12

Volatilization Losses of Lindane Applied to the Surface of Soils

Exactly 0.05 grams of oven-dried adsorbent were weighed into stainless steel planchets and spread uniformly over the bottom. Then 200 µl of a benzene solution containing 50 µg/ml γ-BHC (with 5 µc/l of C^{14} uniform-labeled γ-BHC) was applied to the adsorbent evenly. The applied solution was permitted to evaporate. One hour following the liquid evaporation, the experimental planchets along with blanks were counted for the first time. Counting was performed on a Chicago-Nuclear gas-flow counter. The average of five ten-minute counts was used for the gross cpm. Between counting periods the planchets were placed in an appropriate area where evaporation could occur freely, and occasionally with air movement for a few hours at a time. Table A-8 gives the average net cpm and the estimated amount of lindane residual on the three adsorbents in terms of µg per gram of adsorbent for each counting time.

Table A-8

Residual Lindane on Adsorbent Surface after Differing Time Periods Following Application of a 50 mg/l Benzene Solution

Time Period after drying of applied solution	Ca-Venado clay		Ca-Bentonite		Basic Alumina		Standard blank (no adsorbent)	
	C	R	C	R	C	R	C	R
1 hour	225	150	241	160	153	100	266	180
16 hours	151	100	177	120	127	85	47	31
2 days	101	68	114	76	63	42	22	15
9 days	49	32	33	22	8.6	6	4.0	3
38 days	19	13	20	13	4.3	3	2.7	2
90 days	13	9	13	9	3.2	2	1.6	1

C = net cpm.
R = estimated residual lindane on the basis of µg/gm.

FIGURE A-1

LANGMUIR PLOTS OF γ-BHC-WATER SYSTEMS

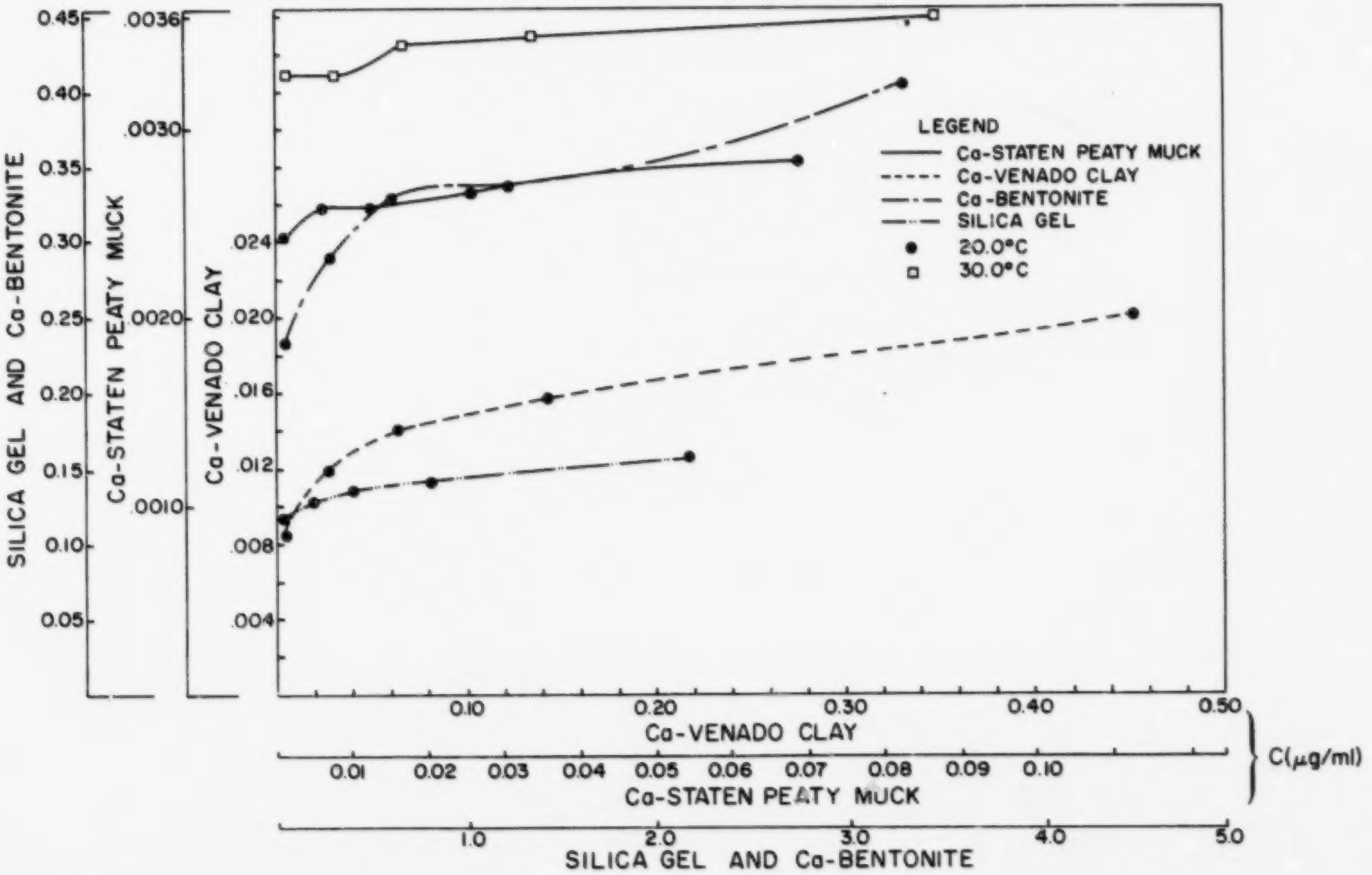


FIGURE A-2

LANGMUIR PLOTS OF β-BHC-WATER SYSTEMS

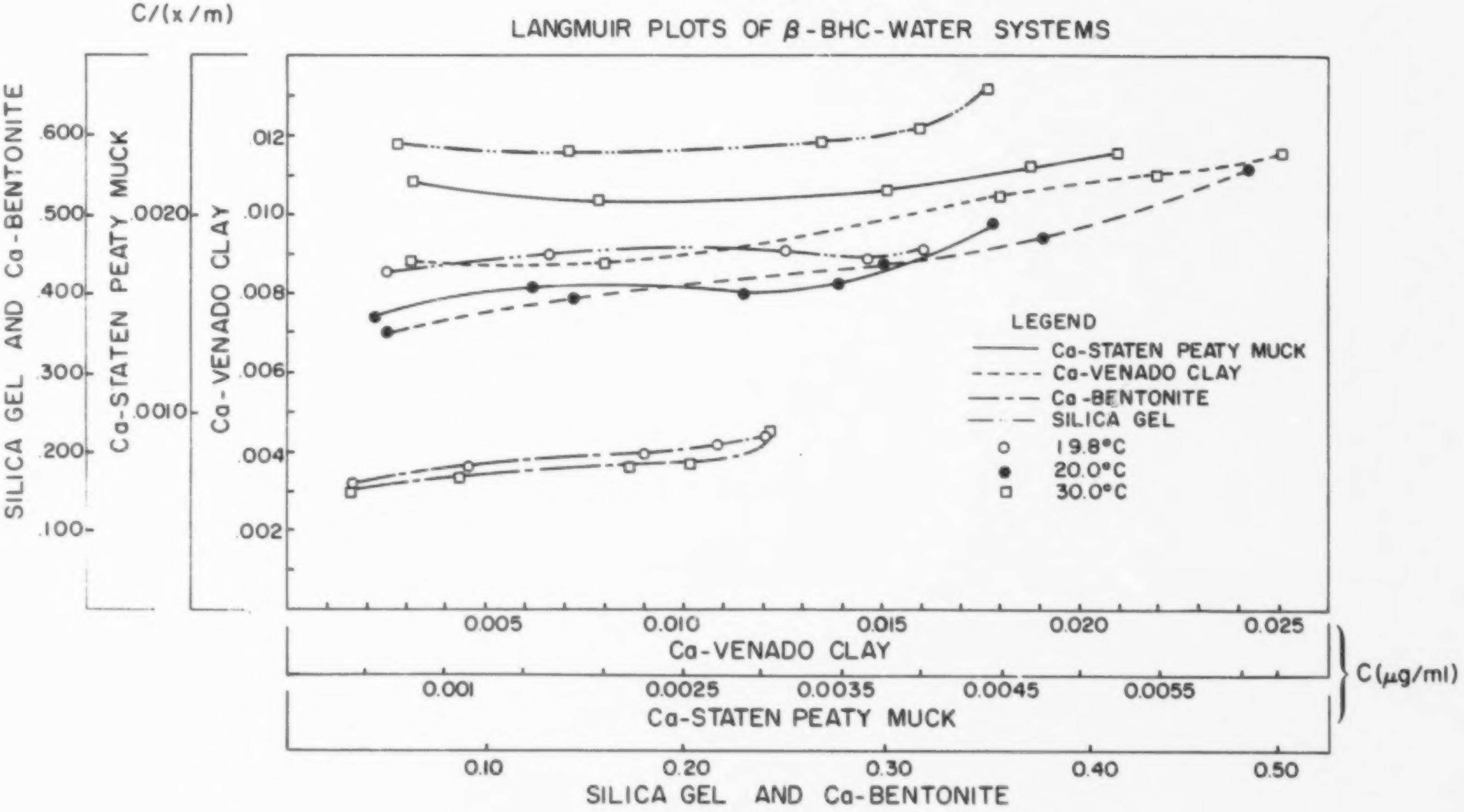


FIGURE A-3

LANGMUIR PLOTS OF γ-BHC-HEXANE SYSTEM

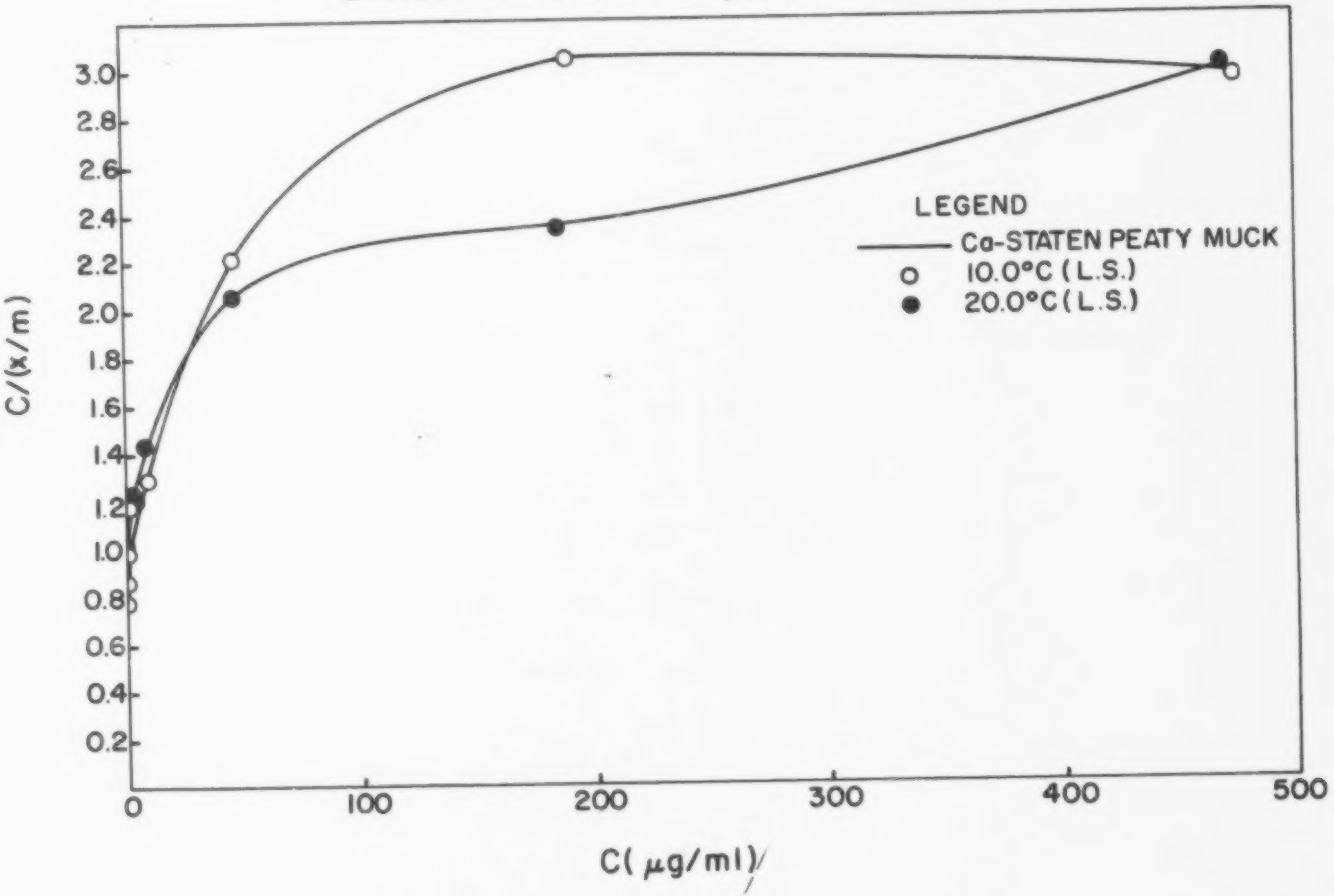


FIGURE A-4

EXTRAPOLATIONS FOR γ-BHC-STATEN PEATY MUCK-WATER SYSTEM

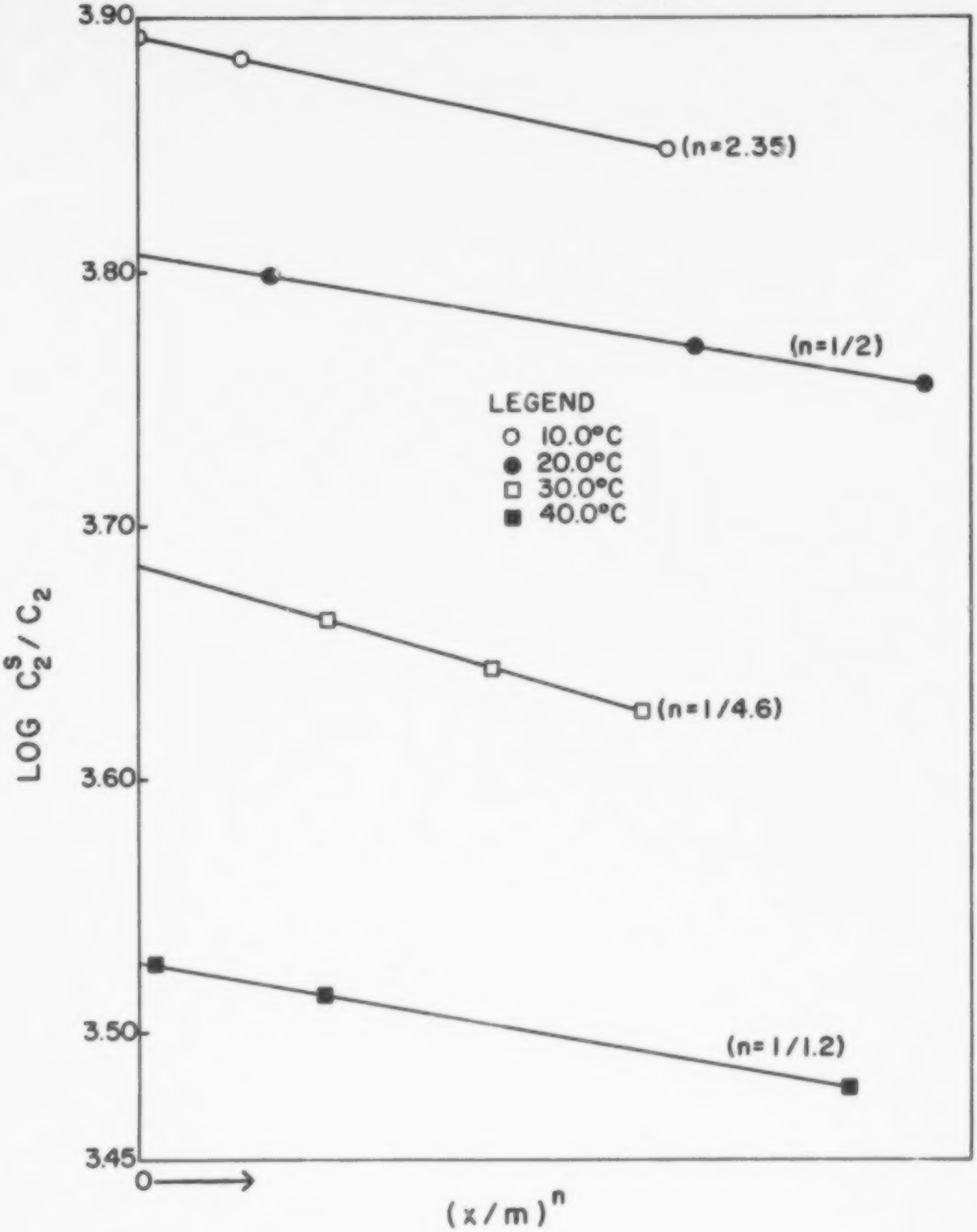


FIGURE A-5

EXTRAPOLATIONS FOR γ-BHC-WATER SYSTEMS WITH BENTONITE AND SILICA GEL

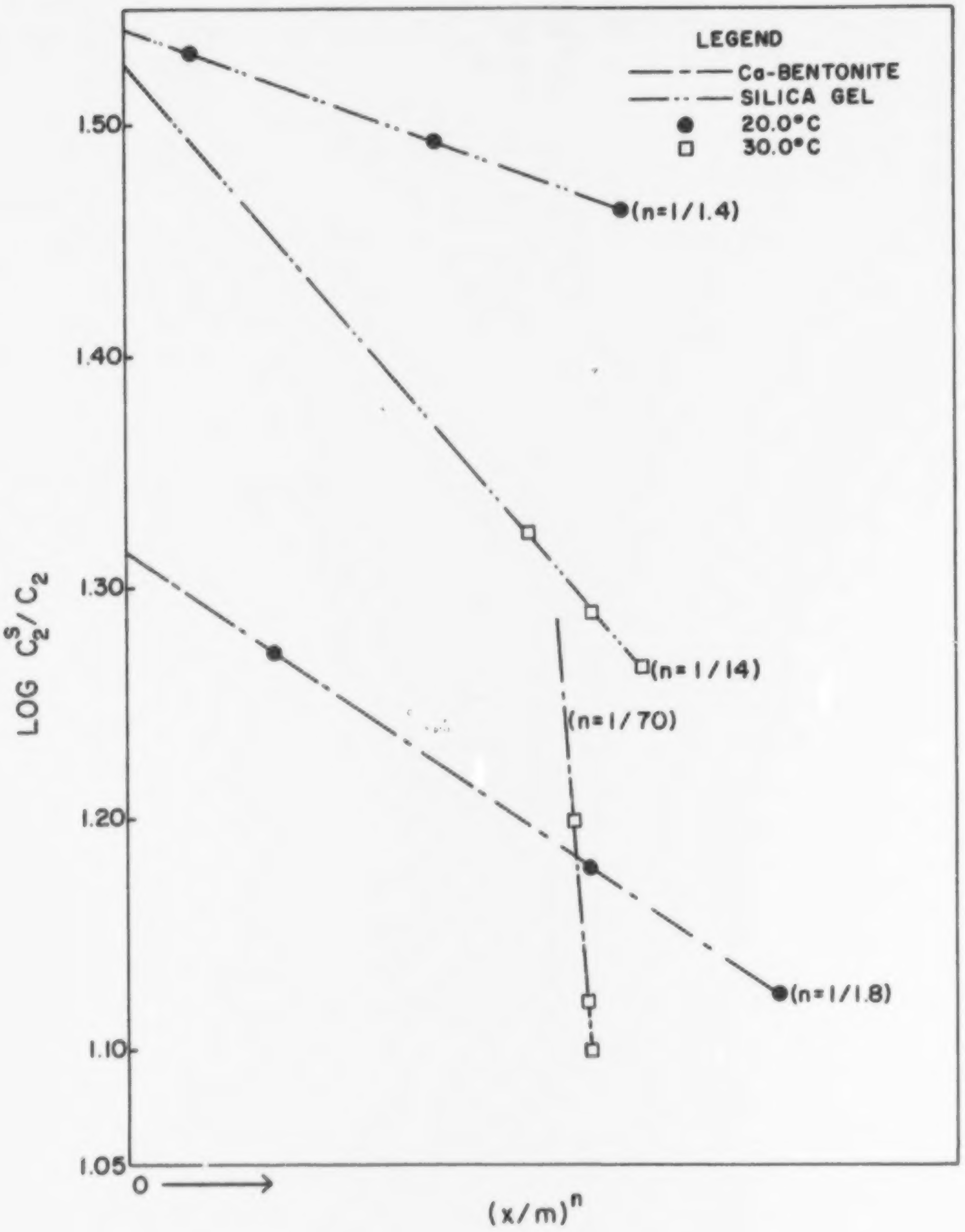


FIGURE A-6

EXTRAPOLATIONS FOR γ-BHC-STATEN PEATY MUCK-HEXANE SYSTEM

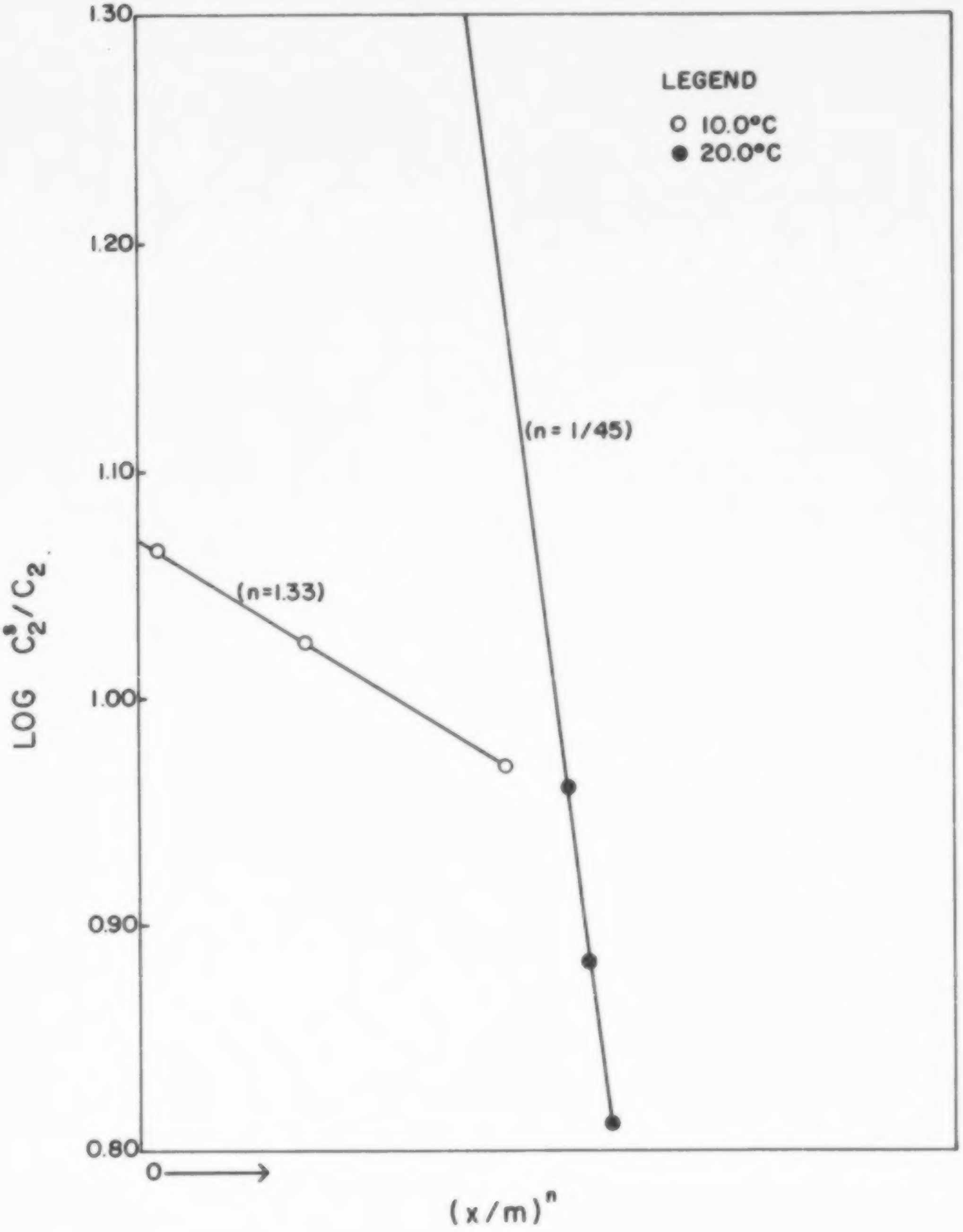


FIGURE A-7

EXTRAPOLATIONS FOR β-BHC-SILICA GEL-WATER SYSTEM

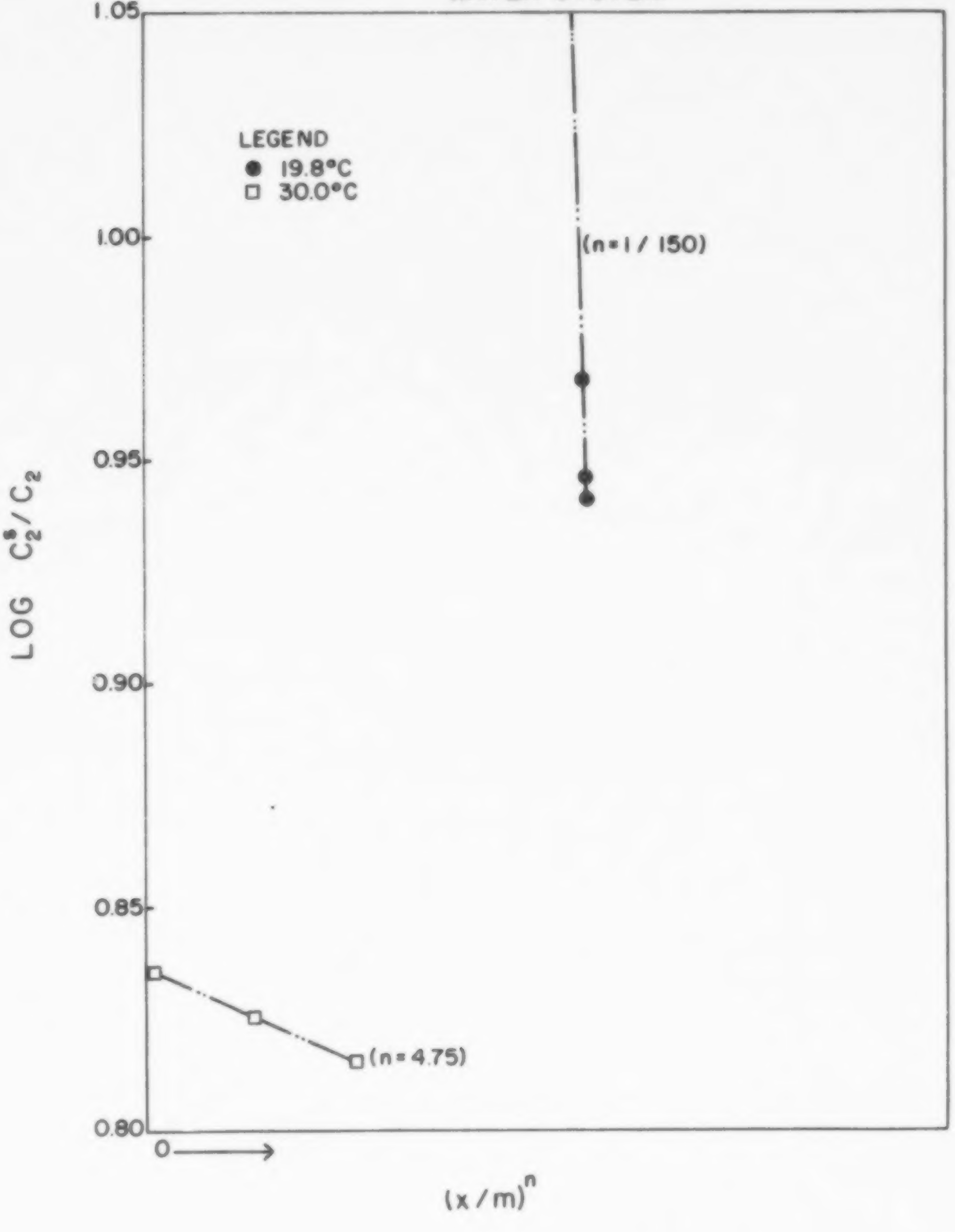


FIGURE A-8

VARIATION OF γ_2^S WITH x/m FOR β-BHC AQUEOUS SYSTEMS AT 20°C

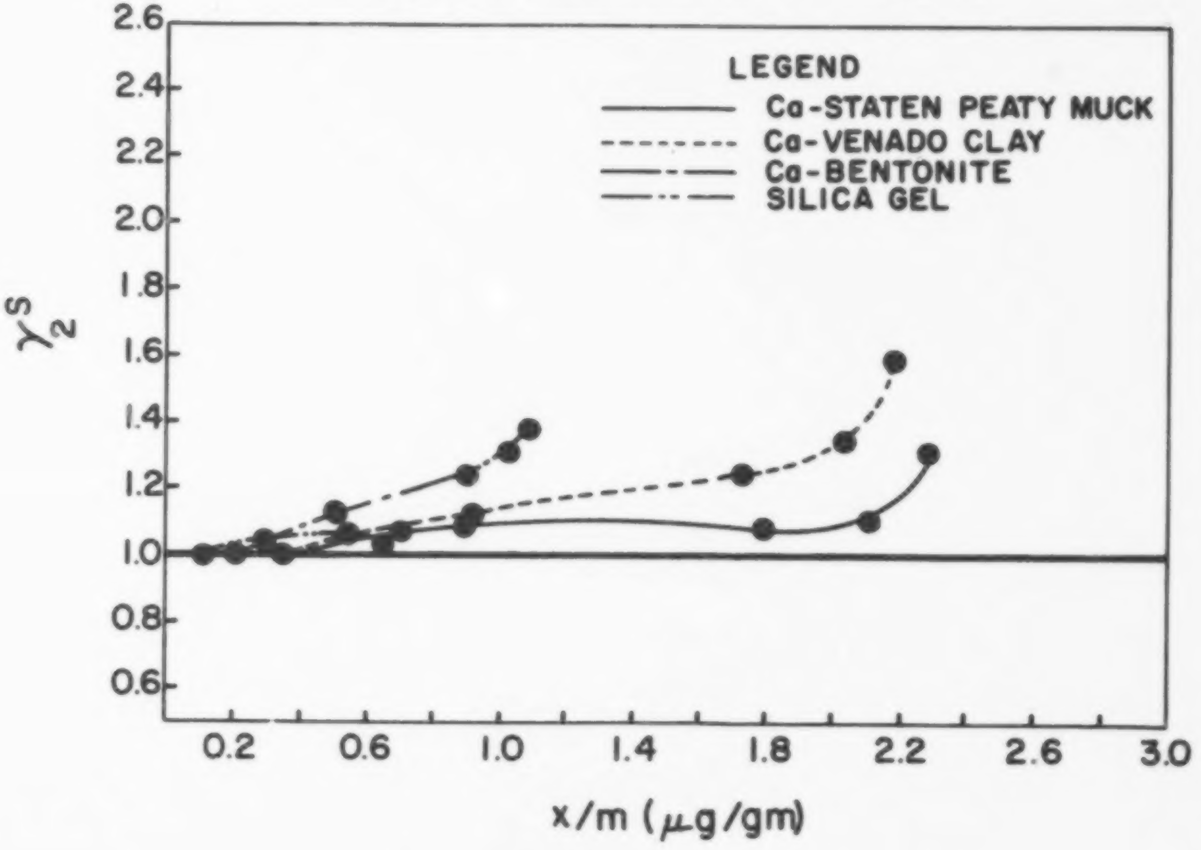


FIGURE A-9a

VARIATION OF $-A_T\Delta\sigma$ WITH m_2^s/m_2 FOR AQUEOUS β-BHC SYSTEMS

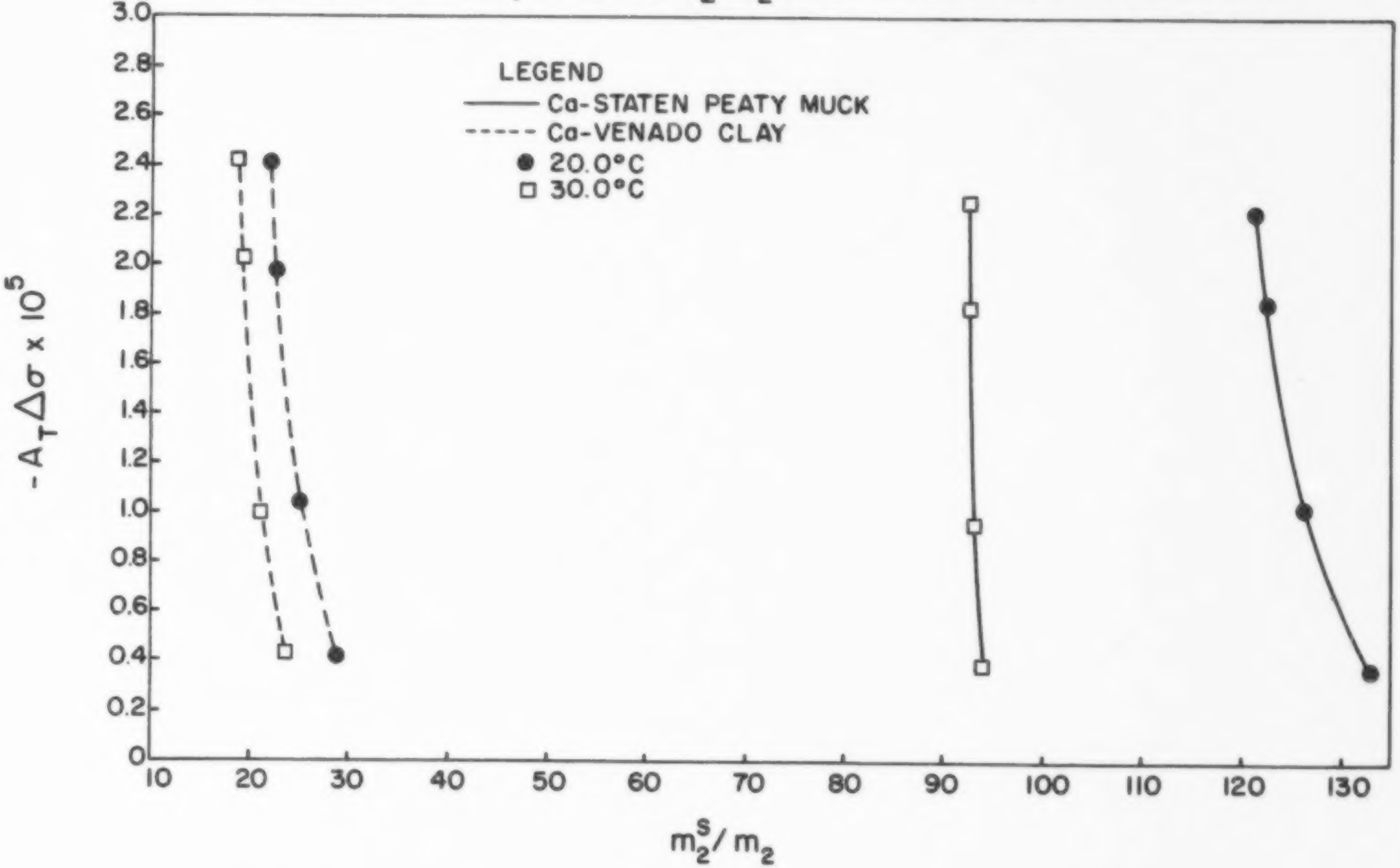


FIGURE A - 9b

VARIATION OF $-A_T\Delta\sigma$ WITH $(m_2^S/m_2)m_0$ FOR AQUEOUS β-BHC SYSTEMS

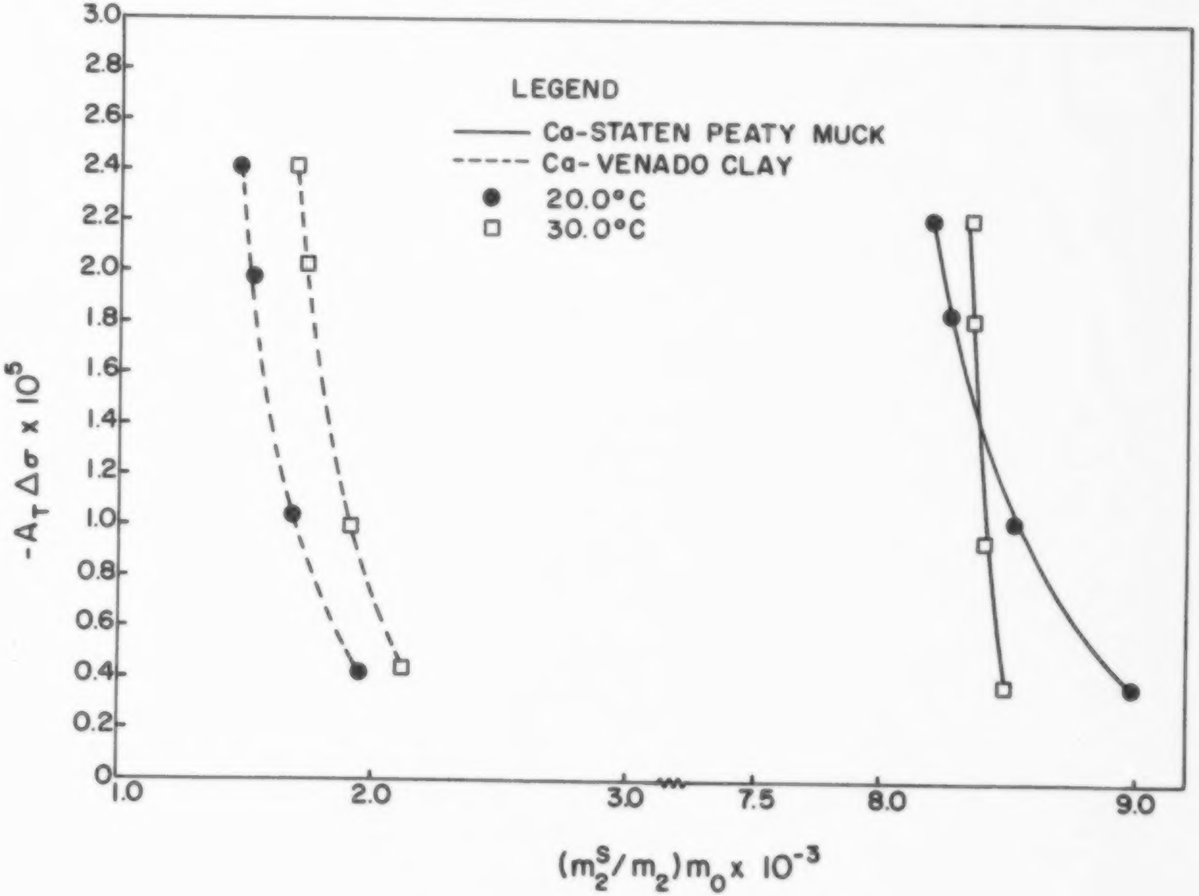


FIGURE A-10a

VARIATION OF $-A_T\Delta\sigma$ WITH m_2^s/m_2 FOR AQUEOUS β-BHC SYSTEMS

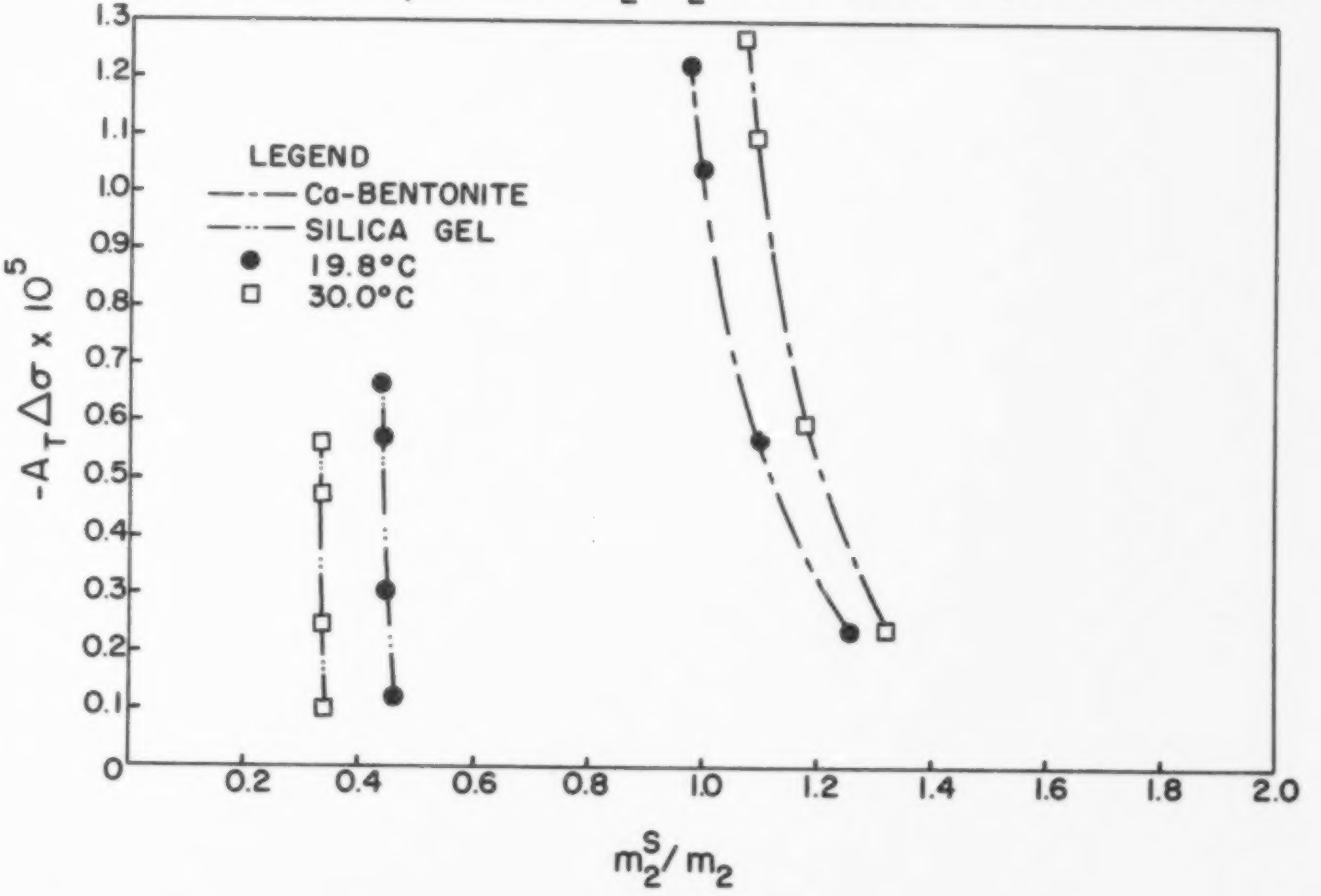


FIGURE A - 10b

VARIATION OF $-A_T \Delta\sigma$ WITH $(m_2^S/m_2)m_0$ FOR AQUEOUS β-BHC SYSTEMS

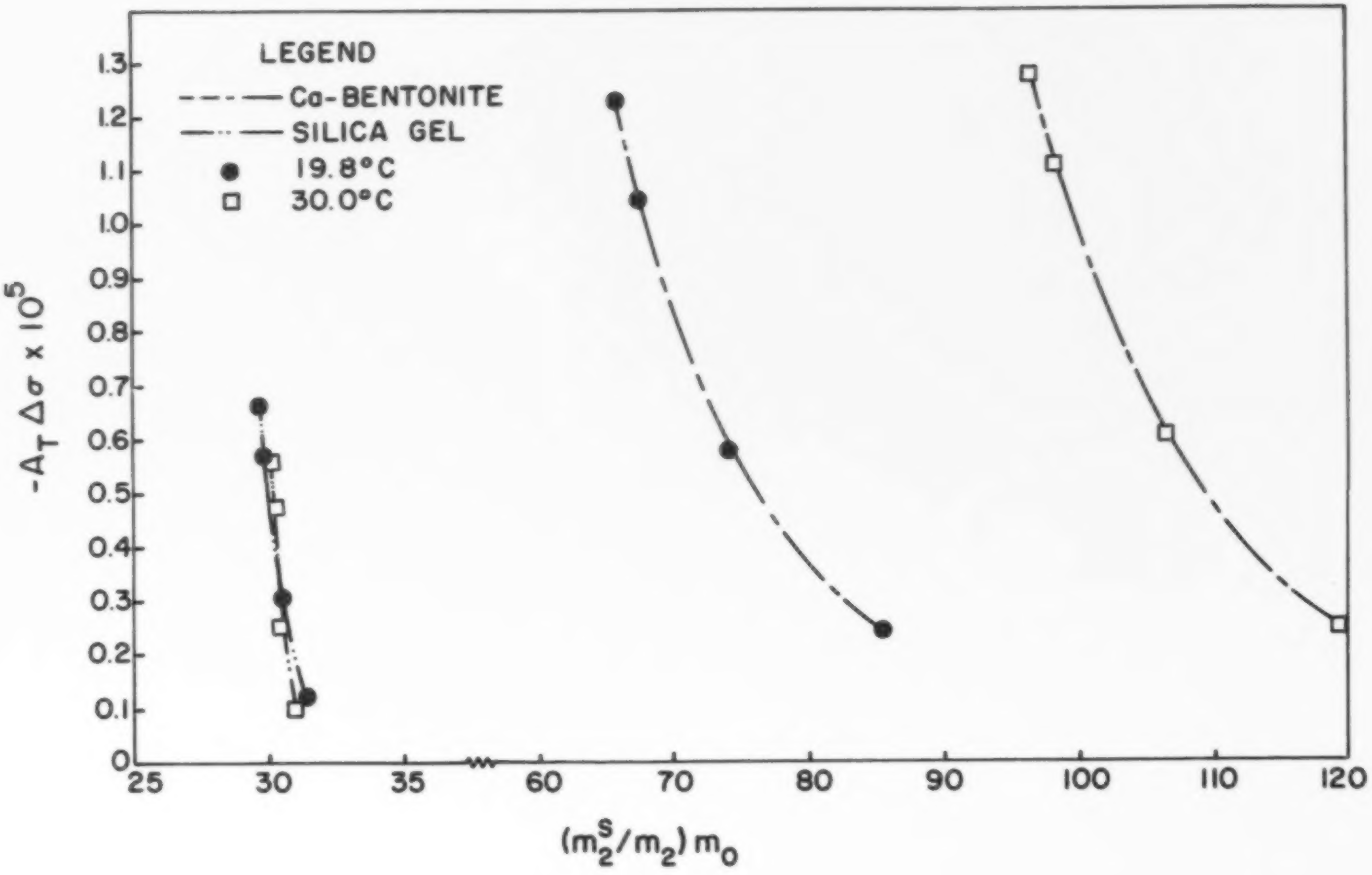


FIGURE A-11a

VARIATION OF $-A_T \Delta\sigma$ WITH m_2^S/m_2 FOR THE γ-BHC-STATEN PEATY MUCK-HEXANE SYSTEM

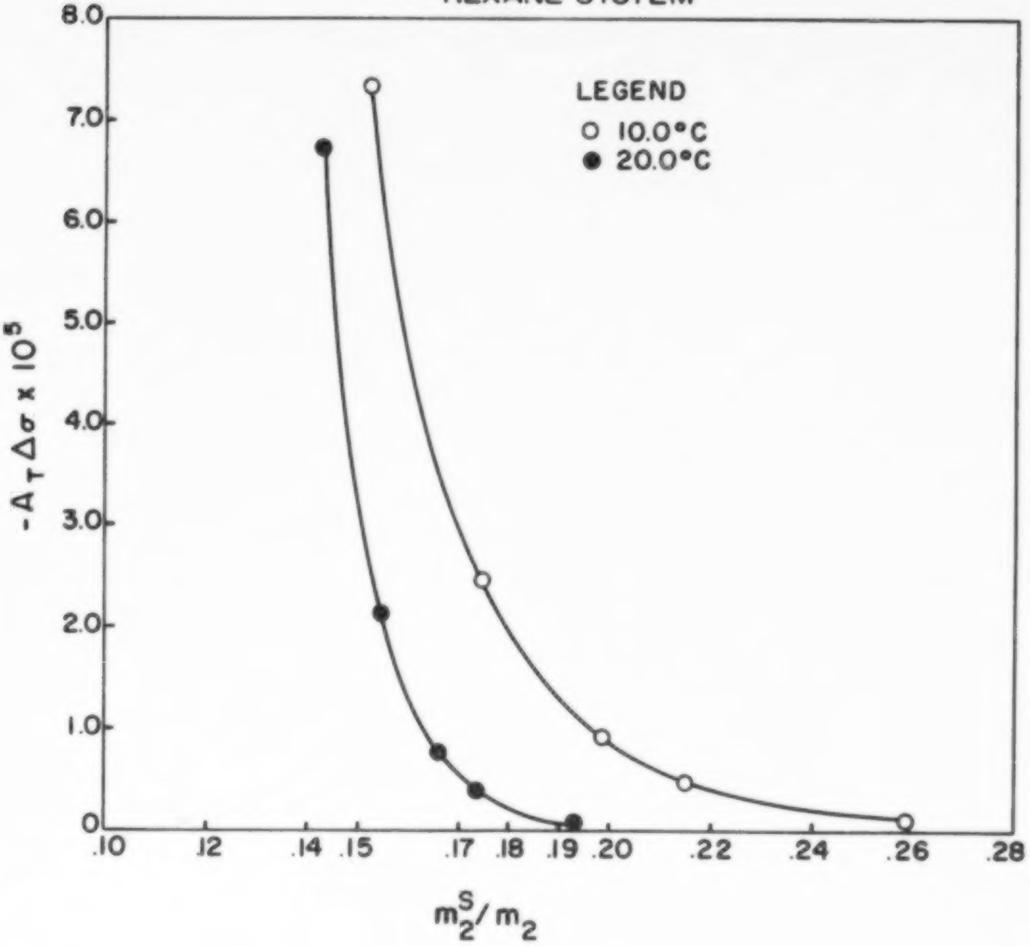
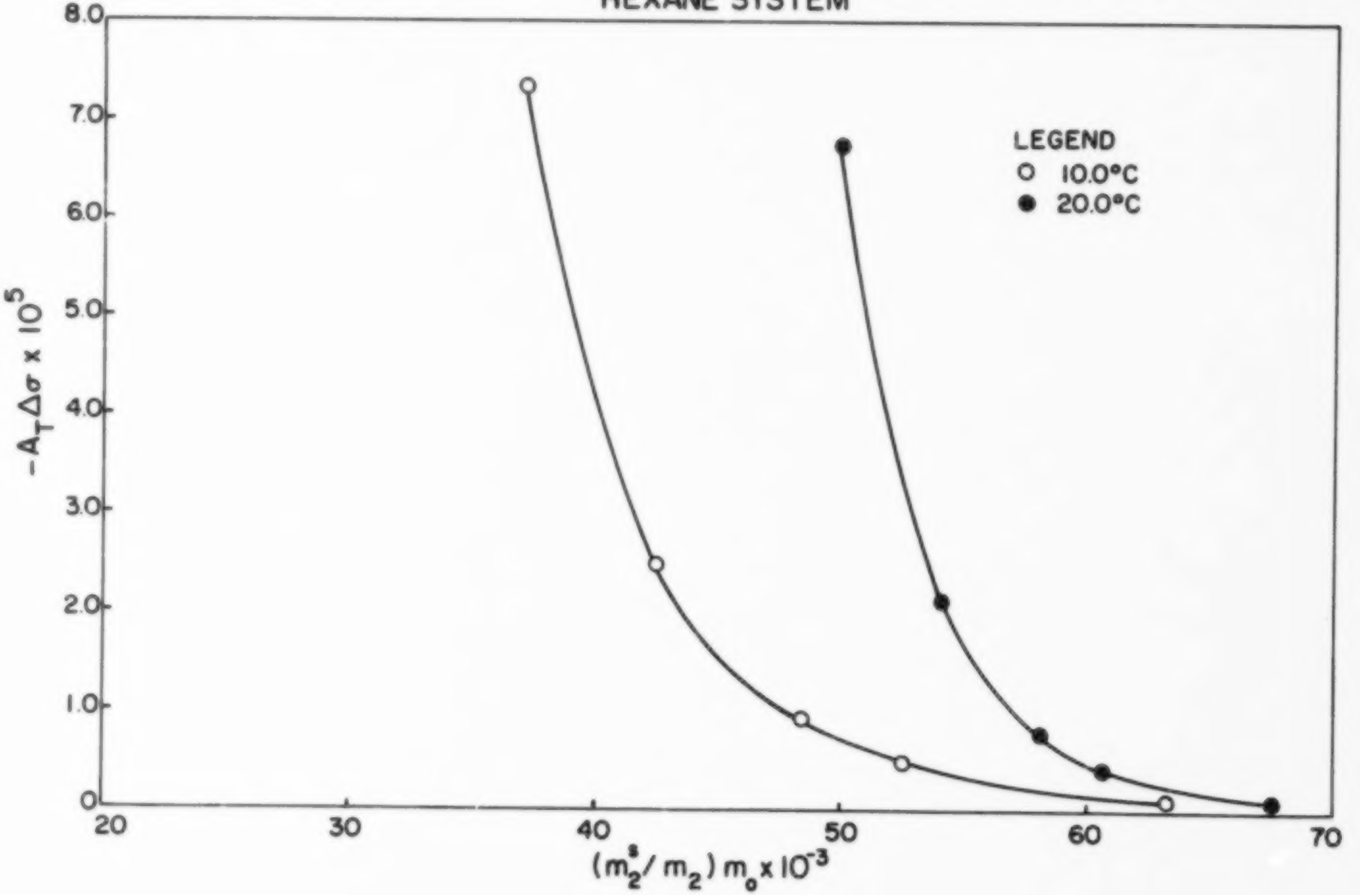


FIGURE A-11b

VARIATION OF $-A_T \Delta\sigma$ WITH $(m_2^s/m_2)m_0$ FOR THE γ-BHC- STATEN PEATY MUCK-HEXANE SYSTEM



BIBLIOGRAPHY

1. Armour Research Foundation of Illinois Institute of Technology, Crystallographic data 20. γ-Hexachlorocyclohexane. *Analytical Chemistry* 21(7), 882-3 (1949).

2. Aronoff, Sam, *Techniques of Radiobiochemistry*, The Iowa State College Press, Ames, Iowa, 1956.

3. Bailey, G. W., and J. L. White, Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. *Agricultural and Food Chemistry* 12(4), 324-332 (1964).

4. Balson, E., Vapor pressure measurement, III. Vapor pressure of DDT and other slightly volatile substances. *Transactions of the Faraday Society* 43, 54 (1947).

5. Barrow, Gordon M., *Physical Chemistry*, Mc-Graw-Hill Book Co., Inc., 1961.

6. Bering, B. P., and V. V. Serpinsky, Calculation of the heat and entropy of adsorption from a single isotherm. *Akademiia nauk SSSR Doklady, Novaia Seriia*. *Akademiia Nauk SSSR Proceedings*. *Section: Physical Chemistry* 114, 417-19 (1957).

7. Bower, C., and F. Gschwend, Ethylene glycol retention by soils as a measure of surface area and interlayer swelling. *Soil Science Society of America Proceedings* 16, 342-345 (1952).

8. Bradley, W. F., Molecular associations between montmorillonite and some polyfunctional organic liquids. *Journal of the American Chemical Society* 67, 975-981 (1945).

9. Brass, C. L., and G. W. Ware, BHC translocation from treated soil and the effect on growth of red clover. *Journal of Economic Entomology* 53(1), 110-113 (1960).

10. Brindley, G. W., R. Bender, and S. Ray, Sorption of non-ionic aliphatic molecules from aqueous solutions on clay minerals, Clay-organic studies - VII. *Geochimica et Cosmochimica Acta* 27, 1129-1137 (1963).

11. Cassidy, H. G., *Adsorption and Chromatography*. *Technique of Organic Chemistry*, *Volume V*, Editor, A. Weissburger, Interscience Publishers, Inc., 1951.

12. Chase, Grafton D., *Principles of Radioisotope Methodology*, Burgess Publishing Company, Minneapolis, Minnesota, 1959.

13. Coffey, S. (Editor), *Rodd's Chemistry of Carbon Compounds*, Second edition, Volume II, *Alicyclic Compounds*, Elsevier Publishing Co., 1965.

14. Daviaud, R. and G. Viel, Dehalogenation of some chlorinated insecticides. Phytiat.-Phytopharm. 3, 29-34 (1952).

15. Dyne, P., and N. Sagert, Exchange reactions in the radiolysis of adsorbed hydrocarbons. Nature 210, 1153-54 (1966).

16. Eberly, P. E., Hydrocarbon adsorption studies at low pressures on the Na- and H- forms of synthetic mordenite. Journal of Physical Chemistry 67(11), 2404-11 (1963).

17. Eckstein, Z., Z. Mazankowa, and J. Orlowski, Continuous catalytic process for dehydrochlorination of inactive isomers of hexachlorocyclohexane. Przemysl Chem. 41, 705-8 (1962), as abstracted in Chem. Abstracts 59, 3794d (1963).

18. Elias, H., K. H. Lieser, and H. W. Kohlschütter, Radiochemical investigation of the isomerization of 1,2,3,4,5,6-hexachlorocyclohexane. Chem. Ber. 93, 2128-37 (1960), as abstracted in Chem. Abstracts 55, 2514 (1961).

19. Everett, D. H., Thermodynamics of adsorption from solution. Part I. Perfect Systems. Transactions of the Faraday Society 60, 1803-1813 (1964).

20. Everett, D. H., Thermodynamics of adsorption from solution. Part II. Imperfect systems. Transactions of the Faraday Society 61, 2478-2495 (1965).

21. Frissel, M. J., The Adsorption of Some Organic Compounds, Especially Herbicides, on Clay Minerals. Ph.D. Thesis, University of Wageningen, 1961.

22. Fu, Y., R. S. Hansen, and F. E. Bartell, Thermodynamics of adsorption from solutions. I. The molality and activity coefficients of adsorbed layers. Journal of Physical Chemistry 52, 374-386 (1948).

23. Gargantini, H., O. Gianotti, and R. DeTella, Leaching of BHC (gamma isomer) from a Bauru sandy soil. Bragantia 16, 73-79, as abstracted in Soils and Fertilizers 22(3), 1343 (1959).

24. Giles, C. H., T. H. MacEwan, S. N. Nakhwa, and D. Smith, Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific areas of solids. Journal of the Chemical Society 1960, 3973-3993 (1960).

25. Greenland, D. J., R. H. Laby, and J. P. Quirk, Adsorption of amino acids and peptides by montmorillonite and illite. Transactions of the Faraday Society 61, 2013-35 (1965).

26. Guillemin, C. L., Separation of isomers of hexachlorocyclohexane by gas chromatography. Anal. Chim. Acta 27, 213-18 (1962), as abstracted in Chem. Abstracts 58, 889a (1963).

27. Hadaway, A. B., and F. B. Barlow, Studies on aqueous suspensions of insecticides. Bulletin of Entomological Research 49, 315-354 (1958).

28. Haller, H. L., and C. V. Bowen, Basic facts about benzene hexachloride. Agricultural Chemicals 2(1), 15-17 (1947).

29. Hanack, Michael, Conformation Theory, Academic Press, 1965.

30. Hansen, R. S., and U. H. Mai, Idealized models for adsorption from solution. I. Van der Waals adsorption from regular solutions. Journal of Physical Chemistry 61, 573-577 (1957).

31. Harris, C. I., Adsorption and Desorption of Herbicides by Soil. Ph.D. Thesis, Purdue University, 1962.

32. Hendricks, S. B., Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to Van der Waals forces. Journal of Physical Chemistry 45, 65-81 (1941).

33. Hill, T. L., Statistical mechanics of adsorption. V. Thermodynamics and heat of adsorption. Journal of Chemical Physics 17(6), 520-535 (1949).

34. Hoffmann, R. W., and G. W. Brindley, Adsorption of non-ionic aliphatic molecules from aqueous solutions on montmorillonite, Clay-organic studies II. Geochimica et Cosmochimica Acta 20, 15-29 (1960).

35. Hughes, E. D., C. K. Ingold, and R. Pasternak, Mechanism of elimination reactions. Part XVIII. Kinetics and steric course of elimination from isomeric benzene hexachloride. Chemical Society of London, Journal 1953, 3832-39 (1953).

36. Jackson, M. L., Soil Chemical Analysis--Advanced Course, University of Wisconsin, Madison, Wisconsin, 1956.

37. Jameson, H. R., and F. C. Peacock, The persistence of crude benzene hexachloride in the soil. Journal of the Science of Food and Agriculture 3, 78-82 (1952).

38. Jurinak, J. J., and D. H. Volman, Application of the Brunauer, Emmett and Teller equation to ethylene dibromide adsorption by soils. Soil Science 83(6), 487-496 (1957).

39. Jurinak, J. J., and D. H. Volman, Thermodynamics of ethylene dibromide vapor adsorption by Ca-montmorillonite and Ca-kaolinite. Soil Science 86(1), 6-12 (1958).

40. Jurinak, J. J., and D. H. Volman, Adsorption of n-butane by kaolinite and montmorillonite: Phase changes in the monolayer region. Soil Science Society of America Proceedings 23(1), 25-28 (1959).

41. Jurinak, J. J., and D. H. Volman, Acid-base interaction in the adsorption of olefins on aluminum kaolinite. Journal of Physical Chemistry 63, 1373-6 (1959).

42. Kipling, J. J., Adsorption from Solutions of Non-Electrolytes, Academic Press, 1965.

43. Klosa, Josef, Stability of gammexane. Archiv der Pharmazie und Berichte der Deutschen Pharmazeutischen Gesellschaft 286, 216-17 (1953), as abstracted in Chem. Abstracts 48, 4165c (1954).

44. Klotz, I. M., Chemical Thermodynamics, W. A. Benjamin, Inc., New York, 1964.

45. Kodera, K. and Y. Onishi, The molecular cross-sectional areas for the determination of specific surface areas of solids. I. Carbon black. Bulletin of the Chemical Society of Japan 32, 356-61 (1959).

46. Krishnamurti, K., and W. F. Mirza, Relation between solubility and adsorbability of substances. Die Naturwissenschaften 46(18), 531 (1959).

47. Kurlyandskaya, I. I., and Yu. M. Martynov, Adsorption of sparingly soluble substances. Russian Journal of Physical Chemistry 38(4), 571-573 (1964).

48. Lichtenstein, E. P., Movement of insecticides in soils under leaching and non-leaching conditions. Journal of Economic Entomology 51, 380-383 (1958).

49. Lichtenstein, E. P., L. J. DePew, E. L. Eshbaugh, and J. P. Sleesman, Persistence of DDT, aldrin, and lindane in some midwestern soils. Journal of Economic Entomology 53(1), 136-142 (1960).

50. Lichtenstein, E. P., and K. R. Schulz, Breakdown of lindane and aldrin in soil. Journal of Economic Entomology 52(1), 118-124 (1959).

51. Lichtenstein, E. P., and K. R. Schulz, Persistence of some chlorinated hydrocarbon insecticides as influenced by soil types, rate of application and temperature. Journal of Economic Entomology 52(1), 124-131 (1959).

52. Lind, E. L., M. E. Hobbs, and P. M. Gross, The electric moments of five of the isomeric hexachlorocyclohexanes. Journal of the American Chemical Society 72, 4474-77 (1950).

53. MacEwan, D. M. C., X-ray identification and structure of clay minerals. The Montmorillonite Minerals, pp. 86-137, The Mineralogical Society of Great Britain Monograph, 1951.

54. MacPhee, Chisholm, and MacEachern, The persistence of certain pesticides in the soil and their effect on crop yields. Canadian Journal of Soil Science 40, 59-62 (1960).

55. McGregor, R., and B. Milićević, On the enthalpy-entropy relationship. Nature 211, 523-525 (1966).

56. Menzie, C. M., Metabolism of Pesticides, Special Scientific Report -- Wildlife no. 96, U. S. Department of Interior, Fish and Wildlife Service, Washington, D. C., 1966.

57. Morino, Y., I. Miyagawa, and T. Oiwa, Botyu Kagaku 15, 181 (1950).

58. Mulla, Mir S., Loss of activity of chlorinated hydrocarbon insecticides in soil as measured against the eye gnat. Journal of Economic Entomology 53(5), 785-87 (1960).

59. Nakajima, M., K. Inagaki, and T. Tati, Utilization of the inactive isomers of benzene hexachloride. II. Reaction of benzene hexachloride with metallic dust. Botyu Kagaku 16, 107-11 (1951), as abstracted in Chem. Abstracts 46, 3962 (1952).

60. Nose, K., T. Suzuki, and K. Fukunaga, P-substituted nitrobenzene adsorption on soil. [Abstract.] Soil Science and Plant Nutrition 10(3), 45 (1964).

61. Nose, K., T. Suzuki, and K. Fukunaga, Pentachlorophenol (PCP) adsorption on soil. (Part I) Variety of PCP adsorption. [Abstract.] Soil Science and Plant Nutrition 10(1), 42 (1964).

62. Nose, K., T. Suzuki, and K. Fukunaga, Pentachlorophenol (PCP) adsorption on soil. (Part 2) Effects of humus, pH, and exchangeable cations upon PCP adsorption on soil. [Abstract.] Soil Science and Plant Nutrition 10(2), 45 (1964).

63. Nose, K., T. Suzuki, and K. Fukunaga, PCP adsorption on soil. (Part 3) Some correlation of PCP adsorption, heat of wetting, and cation exchange capacity. [Abstract.] Soil Science and Plant Nutrition 10(3), 43 (1964).

64. Nose, K., T. Suzuki, and K. Fukunaga, Adsorption of phenols on fuller's earth. [Abstract.] Soil Science and Plant Nutrition 10(4), 46 (1964).

65. Oda, N., K. Norishima, and H. Uchijima, Determination of α-, β-, γ-, and δ-isomers of benzene hexachloride by gas chromatography. Bunseki Kagaku 12(5), 461-6 (1963), as abstracted in Chem. Abstracts 59, 14512c (1963).

66. Odumanova-Dunaeva, G. A., and K. I. Kozlova, Penetration of chloroorganic insecticides through the roots and their translocation within plants. Botan. Zh. 49(9), 1272-78 (1964), as abstracted in Chem. Abstracts 62, 3342f (1965).

67. Orlowski, J. and Z. Eckstein, Catalytic and pyrolytic dehydrochlorination of the pure α-, β-, γ-, and δ-isomers of hexachlorocyclohexane. Bull. Acad. Polon. Sci., Ser. Sci. Chim. 9(10), 619-25 (1961), as abstracted in Chem. Abstracts 60, 1611g (1964).

68. Orlowski, J., Z. Mazankowa, and Z. Eckstein, Utilization of inactive isomers of hexachlorocyclohexane. VII. Catalytic activity of some organic bases in dehydrochlorination of inactive hexachlorocyclohexane. *Przemysl Chem*. 41(11), 649-51 (1962), as abstracted in *Chem. Abstracts* 59, 3794c (1963).

69. Phillips, F. T., The aqueous transport of water-soluble nematocides through soils. I. The sorption of phenol and ethylene dibromide solutions and the chromatographic leaching of phenol in soils. *Journal of the Science of Food and Agriculture* 15, 444-450 (1964).

70. Press, J. M., Measurement of adsorption of residual insecticides using flowing chromatography. *Bulletin of the World Health Organization* 20, 153-162 (1959).

71. Quivoron, C., and J. Néel, Dipole moments of the 1,2,3,4,5,6-hexachlorocyclohexanes. *Jour. de Chimie Physique et de Physico-chemie Biologique* 61(4), 554-571 (1964).

72. Raghu, K. and I. C. MacRae, Biodegradation of the gamma isomer of benzene hexachloride in submerged soils. *Science* 154, 263-4 (1966).

73. Randolph, N. M., R. D. Chisholm, L. Koblitsky, and J. C. Gaines, *Insecticide Residues in Certain Texas Soils*, Texas Agricultural Experiment Station MP-447, 1960.

74. Riggs, Ralph, Unpublished data, Department of Water Science and Engineering, University of California, Davis, California.

75. Rose, J., *Dynamic Physical Chemistry*, John Wiley and Sons, Inc., New York, 1961.

76. Sazonov, P. V., A. A. Bogdarina, and A. S. Gudkova, Biological activity of aqueous solutions of DDT and HCH. *Trudy Vsesayuz Inst. Zashchity Rastenu* 7, 128 (1956).

77. Schollenberger, C. J., and R. H. Simon, Determination of exchange capacity and exchangeable bases in soil--Ammonium acetate method. *Soil Science* 59(1), 13-24 (1945).

78. Schwabe, Von K., Thermochemical investigations of the isomers of hexachlorocyclohexane. *Zeitschrift für Electrochemie* 60, 151-157 (1956).

79. Schwabe, Von K., and Chr. Legler, Vapor pressures, heats, and entropies of sublimation of the hexachlorocyclohexanes. *Zeitschrift für Electrochemie* 64, 902-5 (1960).

80. Shepard, H., *The Chemistry and Action of Insecticides*, McGraw-Hill Book Co., 1951.

81. Slade, R., The gamma isomer of HCH. *Chemistry and Industry* 64, 314 (1945).

82. Smith, M. S., Persistence of DDT and benzene hexachloride in soils. The Annals of Applied Biology 35, 494-504 (1948).

83. Swanson, C. L. W., F. C. Thorp, and R. B. Friend, Adsorption of lindane by soils. Soil Science 78, 379-388 (1954).

84. Talbert, R. E., and O. H. Fletchall, The adsorption of some s-triazines in soils. Weeds 13(1), 46-52 (1965).

85. Thomas, T. L., Thermodynamics of Adsorption from Solution. Ph.D. Thesis, University of Michigan, 1949.

86. Tsukano, Y., and T. Suzuki, Absorption and translocation of γ-BHC by rice plants. Botyu Kagaku 27(1), 12-16 (1962), as abstracted in Chem. Abstracts 60, 3274f (1964).

87. Upchurch and Mason, The influence of soil organic matter on the phytotoxicity of herbicides. Weeds 10(1), 9-14 (1962).

88. Von Vloten, G. W., Ch. A. Kruissink, B. Strijk, and J. M. Bijvoet, Crystal structure of 'Gammexane.' Nature 162(4124), 771 (1948).

89. Weidhaas, D. E., Adsorption of DDT, Methoxychlor and some related compounds on insecticide dust diluents and carriers. Journal of Economic Entomology 50, 429-435 (1957).

90. West, T. F., and G. A. Campbell, DDT and Newer Persistent Insecticides, Chemical Publishing Co., New York, 1952.

91. Westlake, W. E., and J. P. San Antonio, Insecticide residues in plants, animals, and soils. The Nature and Fate of Chemicals Applied to Soils, Plants, and Animals, pp 105-115, ARS 20-9, U.S.D.A., 1960.

92. Werner, A. E., and M. Waldichuk, Decay of hexachlorocyclohexane in sea water. Journal of the Fisheries Research Board of Canada 18(2), 287-289 (1961).

93. Whetstone, R. R., F. C. Davis, and S. A. Ballard, Interconversion of hexachlorocyclohexane isomers. Journal of the American Chemical Society 75, 1768-9 (1953).

94. Zhdanov, S. P., A. V. Kiselev, V. N. Novikova, and Yu. A. El'tekov, Adsorption of thiophen from solutions by synthetic Na- and Ca-faujasites. Russian Journal of Physical Chemistry 39(7), 915-17 (1965).

Flow of an Aqueous Lindane Solution in a Column of Glass Beads

The displacement of a dilute aqueous salt solution (0.01 N $CaSO_4$) by a saturated aqueous solution of lindane in a glass bead column was studied. It was hoped that by investigating breakthrough curves for the insecticide in such relatively 'inert' porous materials, important relevant information preliminary to studying its transport in natural soils could be obtained. The public health and agricultural significance of the relative ease with which such pesticides are transported through soil is apparent.

Materials

The glass beads used had an average diameter of 200 microns and were designated as 3M "Superbrite" glass beads by the supplier, the Minnesota Mining and Manufacturing Company. The size distribution of the beads is given as 10, 40, 40, and 10 percent retained in U.S. sieve numbers 60, 70, 80, and 100, respectively. The average bulk density of the beads is given as 1.5 and the density of the solid glass is 2.5 grams/cm^3. The composition of these beads is similar to that of ordinary soda-lime-silica window glass (about 20% NaO, 5% CaO, and 75% SiO_2). The supplier states that water will remove some surface alkali from the beads, but that once the surface alkalies are removed there is no noticeable weathering effect.

Reagent grade $CaSO_4$ and boiled distilled water were used to prepare the 0.01 N $CaSO_4$ solution. Lindane as 1,2,3,4,5,6-hexachlorocyclohexane (99-100% gamma isomer) was obtained in powder form from the J. T. Baker Company. Saturated aqueous solutions were prepared by mixing excess lindane powder with boiled distilled water in five-gallon bottles. In order to reduce the possibility of microbial activity in the column, phenol crystals were added to the saturated lindane solutions to give a concentration of approximately 200 ppm phenol.

Methods

Before packing the column, the glass beads were washed several times with distilled water. A lucite column 29 cm long and 7.0 cm in diameter was employed. The column was packed with wet glass beads in a manner such as to keep the number of entrapped air bubbles to a minimum. A fritted glass plate was placed on each end and secured with bolts attached to brackets on the side of the column. The column was set up in a vertical position. Flow took place in an upward direction, so that the bottom fritted glass plate was the inflow plate. Temperature was maintained constant throughout at 24.0 ± 0.5°C. The experiment was carried out with the column fully saturated with solution. The amount of solution entering the column was measured by means of gas burets which also allowed for the maintenance of a constant head. Thus, the flux through the column was maintained fairly constant. Maximum variation of the flux was ± 17%. The buret was filled periodically from a reservoir bottle. Tygon tubing and glass tubing were used to connect the burets to the inflow plate. Rapid change-over from one solution to another was facilitated by using one set, consisting of a buret and a leveling bottle, for each solution. At the time of the change-over, the stopcock at the outflow plate was closed briefly and about 200 ml of the new solution from a leveling bottle flushed out the small reservoir behind the inflow plate. Then the new solution was allowed to flow from its buret through the column at the same flux as employed for the previous solution. A schematic cross-section of this apparatus is given in figure 1 of an article by Nielsen and Biggar.*

The aqueous lindane solution (containing 200 ppm phenol) was not filtered. But the solution in the reservoir bottle was at rest and the glass tube connecting the bottle and the buret did not extend to the bottom of the bottle. Thus, the large undissolved lindane particles did not become a part of the flowing solution.

The effluent was collected in test tubes in an automatic fraction collector. Each tube was filled with 20.0 ml of effluent.

The initial flux was 0.2 cm/hour. This was maintained during the flow of the $CaSO_4$ solution and the subsequent flow of the aqueous lindane solution. After 16 liters of aqueous lindane solution had flowed through the column the flow was terminated. Nineteen days after the termination of this flow, flow of the aqueous lindane solution was initiated again at an average flux of 5.2 cm/hour. After 3.6 liters had passed through the column the flow was reduced to 0.2 cm/hour. Flow was terminated after an additional 1.8 liters had passed through the column.

Analysis of Ca^{++} and Na^{+} in the effluent was done by flame photometry, and analysis for chloride in the effluent was carried out on a Buchler-Cotlove chloridometer. The aqueous effluent solutions were extracted into equal volumes of thiophene-free reagent grade benzene in glass-stoppered test tubes. Analysis for lindane was performed by means of electron-capture gas chromatography. A Wilkins model 600-B Aerograph Hy-Fi gas chromatograph was employed in conjunction with a

---

*Nielsen, D. R., and J. W. Biggar, Miscible displacement in soils: I Experimental information. SSSA Proceedings 25(1): 1-5 (1961).

Honeywell Brown Electronik recorder equipped with a disc integrator. The concentrations of the extracts were determined by evaluating the relative peak areas with the aid of the disc integrator and then relating the peak areas to those for standard lindane solutions in benzene.

Results and Discussion

Figures 1a and 1b show the change in effluent concentration with increasing quantity of aqueous lindane solution passing through the column at a flux of 0.2 cm/hour. The pore volume, V_p (total volume of pores), for this column packed with 200-micron beads has been calculated as 460 ml. It will be noted in figure 1a that just after approximately one pore volume of the lindane solution had flowed into the column displacing the $CaSO_4$ solution, the concentration of Ca^{++} in the effluent began to drop suddenly. And after an additional 300 ml of solution had flowed through the column the concentration of Ca^{++} in the effluent reached a fairly constant low value of 5-7 ppm which held for the remaining part of the flow at low flux (0.2 cm/hour). The curve is displaced slightly to the right of $c/c_o = 0.5$ at V_p, i.e., the Ca^{++} concentration of the effluent was greater than $0.5c_o$ when 460 ml of lindane solution had entered the column. While it is not known why c/c_o did not equal 0.5 at V_p, the displacement of the calcium ion follows a generally expected course. A constant sodium concentration of about 3.0 ppm for the effluent was obtained throughout the flow of 16 liters of lindane solution through the column. The concentration of Ca^{++} and Na^+ in the original aqueous saturated lindane solution was found to be 0.0 and 0.2 ppm, respectively. The excess Na^+ concen-

FIGURE 1a

EFFLUENT CONCENTRATION CURVE - AQUEOUS LINDANE SOLUTION

REPLACING 0.01N $CaSO_4$ SOLUTION

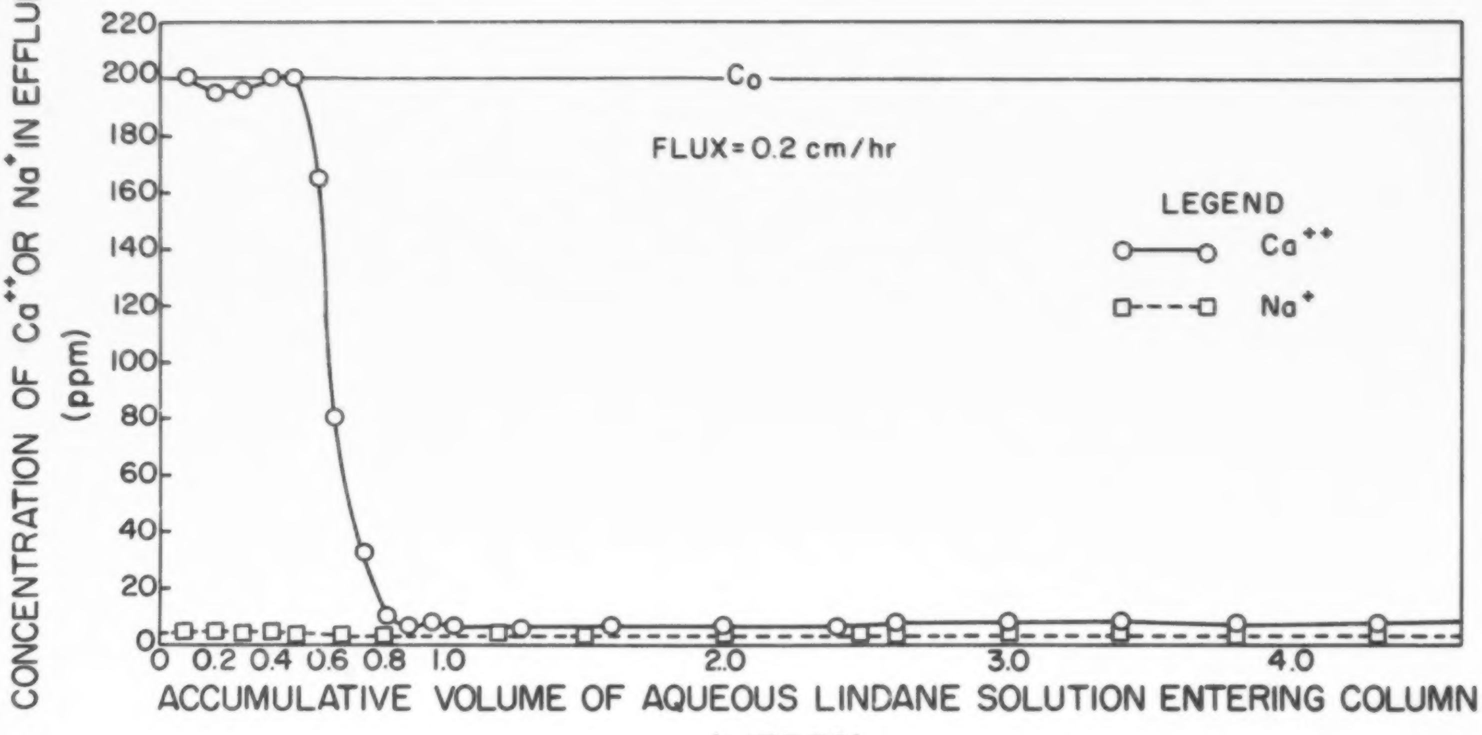
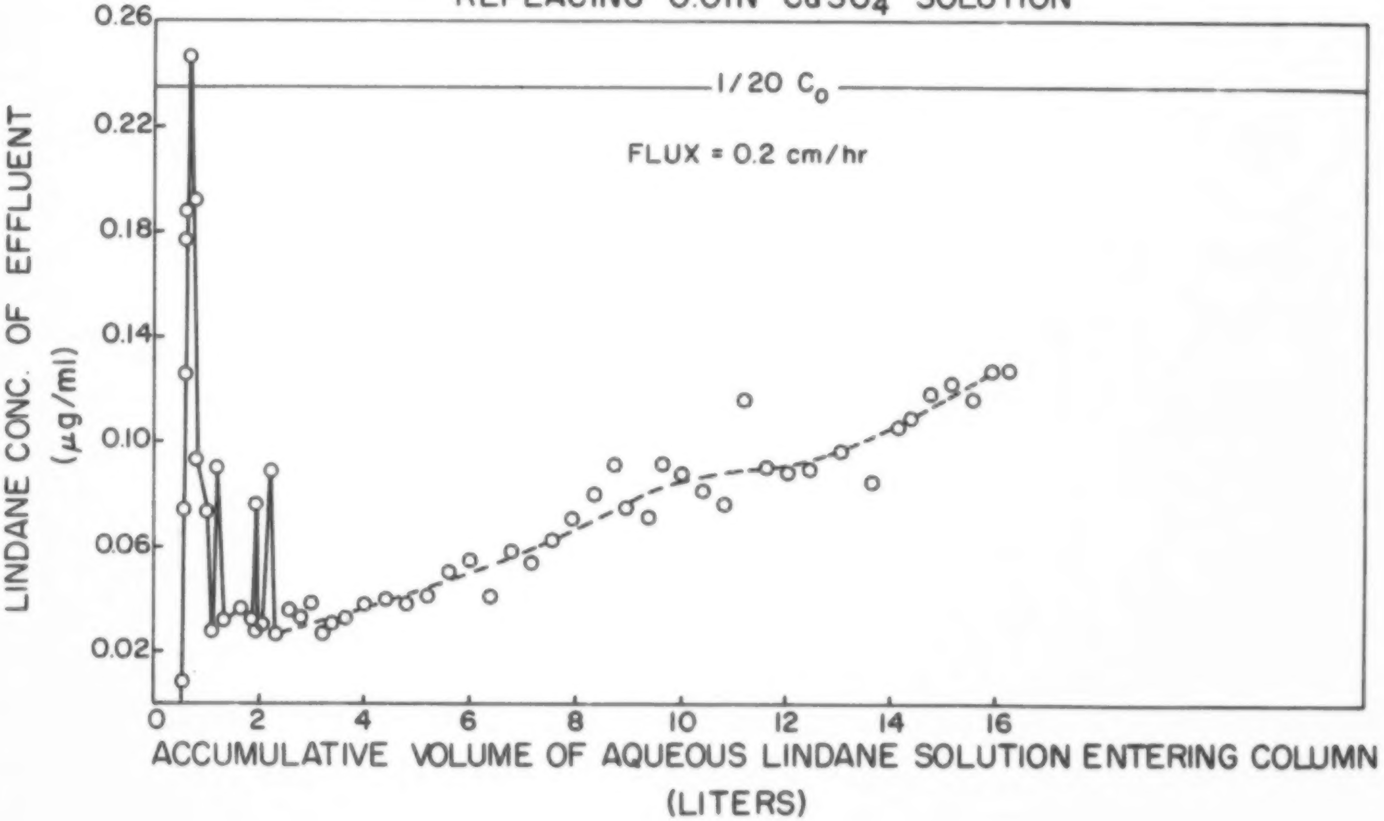


FIGURE 1b

EFFLUENT CONCENTRATION CURVE - AQUEOUS LINDANE SOLUTION

REPLACING 0.01N $CaSO_4$ SOLUTION



tration of the effluent is no doubt due to the removal of NaO from the surface of the glass beads by the flowing solution.

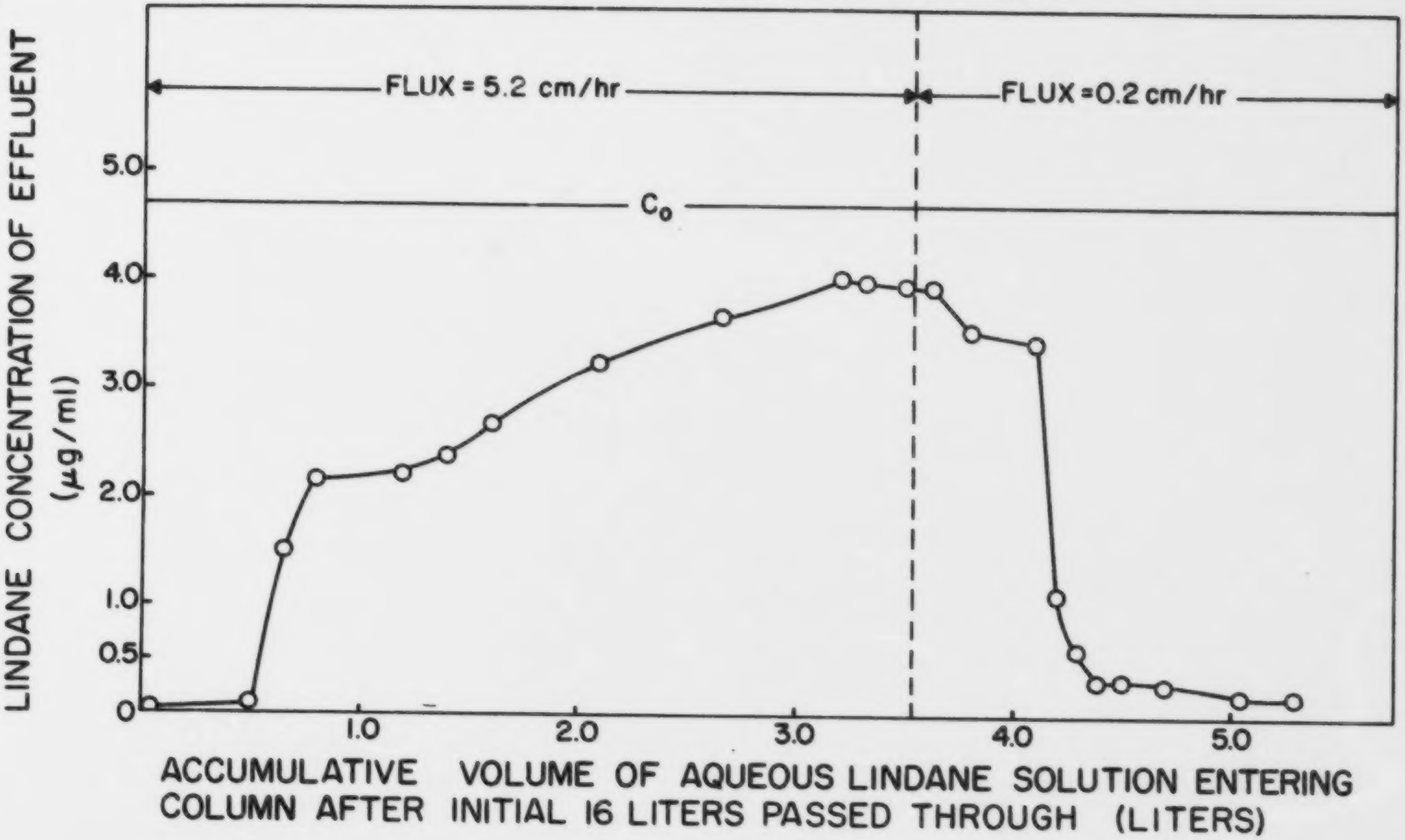
Unlike the reasonable behavior of the Ca^{++} ion upon displacement by a solution containing zero calcium, figure 1b indicates that the concentration of lindane in the effluent follows no predictable course with increasing inflow of lindane solution. The dotted line on the right side of figure 1b represents an attempt to approximate the average rate of increase of lindane concentration in the effluent with increasing solution volume. First of all, it is apparent that the lindane concentration of the effluent at no point from the passage of 0 to 16 liters approached 4.7 µg/ml, the initial lindane concentration of the entering solution (c_o). It is interesting, however, that after one pore volume had passed into the column, the lindane concentration of the effluent rose suddenly from zero to a maximum of 0.247 µg/ml at about 650 ml. Such an increase in effluent concentration is to be expected at that point. But the factors preventing the continued increase of the effluent concentration to c_o are not obvious. It is apparent that some process was taking place which effected the lowering of the lindane concentration from the peak at 650 ml and which permitted only a very gradual and tenuous increase from 0.03 to 0.13 µg/ml from the passage of the 3rd to the 16th liter. The spread of points over this range is probably due to the errors and uncertainties involved in gas chromatographic analysis. It is significant at any rate to observe that after 16,000/460 or almost 35 pore volumes of the lindane solution had passed into the column, the lindane concentration of the effluent was only $0.028c_o$.

The effect of increasing the average flux to 5.2 cm/hour is shown in figure 2. One pore volume after the onset of the flow at this higher flux, the lindane concentration of the effluent began to climb rapidly from 0.10 µg/ml to 2.15 µg/ml at 800 ml. After this, the concentration of lindane is seen to rise more gradually to 4.0 µg/ml when 3.2 liters had passed through the column at the higher flux. It is quite possible that if a further volume of solution had been permitted to flow through the column at the higher flux, the concentration of the effluent would have finally reached c_o. But after 3.54 liters had flowed at the high flux, the flux was reduced to 0.2 cm/hour. The effluent concentration decreased drastically about 560 ml after the flux reduction. And after an additional liter had passed through the column, the effluent concentration had been reduced to 0.20 µg/ml, slightly higher than the final effluent concentration for the initial run at the low flux.

These results indicate that the process acting to withhold the lindane is time-dependent. It would seem that the solution has to be in the column a certain minimum period of time in order for lindane to disappear significantly from solution. A lag approximately equal to the pore volume is evident before the effect of the flux change is realized. It is doubtful that there is any physical interference offered by the fritted glass plates, because saturated lindane solutions have been effectively filtered through fritted-glass filters in this laboratory. The lindane concentration of the filtrate was that expected for a saturated aqueous lindane solution. One would expect that the process operating to reduce the lindane concentration in the effluent was precipitation, adsorption, or decomposition, or some combination of two or all of these.

FIGURE 2

EFFLUENT CONCENTRATION CURVE FOR LINDANE
——EFFECT OF HIGH AND LOW FLUX——



The possibility of losing lindane through volatilization from the collecting test tubes was considered. In some instances the tubes were not stoppered for as much as 12 to 15 hours after their filling. A test was carried out in which fresh saturated aqueous solutions of lindane were placed in test tubes and allowed to remain unstoppered for different time periods. Table 1 shows that probably little or no lindane was lost through volatilization from the tubes over a 24-hour period, depending on how one evaluates the precision of the gas chromatographic analysis. Clearly, volatilization losses from the collecting tubes cannot account for the extreme loss of lindane in the effluent.

Table 1

The Effect upon Final Concentration of the Time of Exposure of Lindane Solution in Test Tubes to the Air

Time period between solution addition and stoppering (hours)	Final lindane concentration (ppm)
0	5.1
1	4.5
3	4.0
5	4.4
7	4.4
9	4.9
12	4.8
24	4.3

From an equilibrium study of the adsorption of aqueous lindane on glass beads, it is clear that adsorption can account for a portion of the disappearance of lindane from the effluent solution at the low flux. The equilibrium study was conducted at 25°C for two time periods, 34 hours and 10 days. Approximately 19 grams of 200-micron glass beads were added to 100 ml of a saturated and half-saturated aqueous solution of lindane in Erlenmeyer flasks and shaken on a wrist-action shaker. After 34 hours, the concentration of the ambient solution for the saturated solution had been reduced from 7.3 to 4.65 ppm. After 10 days the average concentration was 3.47 ppm. It is interesting to note that the average time period a volume of solution would remain in the column at a flux of 0.2 cm/hour was about 6 days. Yet, at the end of 10 days the concentration of the solution in the equilibrium study was about $0.48c_o$ compared to a maximum of $0.053c_o$ for the effluent solution at the low flux. One must conclude that the disappearance of lindane in the column effluent at the low flux is related to the effect of the flow itself and not uniquely to the porous material. The particular pathway of the flow, including entry tubing, inflow plate, etc., may also be important.

On the basis of the adsorption data for the glass beads (assuming that all the lindane lost from solution was adsorbed) one can calculate the maximum amount of lindane that would be adsorbed on the glass beads in the column in equilibrium with a solution of concentration of 4.7 µg/ml, which is the c_o for the column study. On the basis of the 10-day adsorption data, it was calculated that a total of 43.5 mg. or 26.0 µg/gm of lindane would be adsorbed on the glass beads in the column in equilibrium with the c_o solution. In order for this amount of lindane to be adsorbed, a volume of 9.25 liters of c_o solution would have to enter the column. During the initial flow at low flux, a total of 75.2 mg of lindane flowed into the column while only approximately 1.3 mg appeared in the effluent. Even assuming that the maximum calculated amount of 43.5 mg was adsorbed, this leaves an additional

30.4 mg which had disappeared either through decomposition or precipitation.

While the very low concentration of lindane in the effluent at the low flux indicates definite withholding of lindane in the column in excess to that predicted from adsorption data, the opposite appears true for flow at the high flux. From the 34-hour adsorption data it was calculated that 18.9 mg could be adsorbed on the beads in equilibrium with the highest effluent concentration, 4.0 μg/ml, attained at high flux. But only 6.9 mg of lindane were calculated to have been held in the column during the flow of the 3.2 liters at high flux. Thus, at the higher flux, the flowing solution was definitely not in equilibrium with the lindane adsorbed on the beads. Less adsorption took place than predicted by the adsorption study.

The possibility of decomposition of lindane occurring within the column was examined. It would be expected that high alkalinity would be conducive to lindane degradation according to the equation

$$C_6H_6Cl_6 + 3OH^- \longrightarrow C_6H_3Cl_3 + 3H_2O + 3Cl^-. \qquad (1)$$

The pH of a few selected samples of effluent was measured on a Beckman expanded-scale pH meter. Table 2 shows the pH values for the effluent for several periods during the initial flow at low flux. It is clear that the flow through the column has increased the pH of the solution about 1.0 or 1.5 units. This was probably effected in the process of solubilization of the NaO on the surface of the glass beads. From other experiments involving decomposition of lindane, the writer concludes that the pH level of the effluent is not high enough to account for more than 10% of the lindane lost.

Table 2

pH of Effluent Solutions during
the Initial Flow at 0.2 cm/hour

Volume having entered column from time of change over (liters)	pH of effluent
3.2	7.4
4.4	7.3
5.0	7.4
7.0	7.2
9.0	7.0
11.0	7.3
13.0	7.5
15.0	7.4
16.6	7.7
c_o	6.25

If chloride were present in the effluent it would indicate the possibility of decomposition occurring according to equation (1). Analysis for chloride showed that while the c_o solution contained 0.70 ppm chloride, tube no. 837 (after 16.7 liters had entered the column during the initial flow) contained only 0.59 ppm. At the end of the second flow (the last 1.8 liters being allowed to flow at the low flux) the effluent chloride concentration was found to be zero. Thus, there seems to be no evidence to indicate that any significant degree of decomposition occurred in the column.

The contents of the column unfortunately were not analyzed for lindane upon the conclusion of the experiment. But one is left with only one plausible explanation for the almost total disappearance of lindane during flow at low flux. Other workers in this department have shown that the aqueous solubility of lindane is greatly dependent upon the maximum particle size of lindane crystals one permits in solution. As the maximum particle size decreases, the solubility in water decreases considerably. The writer concludes that the column of glass beads acts as a long extended filter during flow at the low flux and the larger-sized lindane particles (say, in the range 0.5 to 5.0 μ effective diameter) are precipitated or filtered out. Only the finer particles which contribute relatively little to the total aqueous solubility of lindane remain in the stream flow and appear in the effluent. At low flux perhaps a settling of the larger particles on the bead surfaces can occur, which cannot take place at the higher flux.

Summary

A saturated solution of lindane in distilled water displaced a 0.01 N $CaSO_4$ solution in flow through a column packed with 200-micron glass beads. At a flux of 0.2 cm/hour, although the concentration of Ca^{++} in the effluent decreased in a predictable manner after the passage of one pore volume of solution, the concentration of lindane in the effluent never became higher than $0.0525c_o$ although a total of 35 pore volumes of lindane solution entered the column. When the flux was increased to 5.2 cm/hour, the concentration of lindane in the effluent rose to 0.46 c_o 1.7 pore volumes after the change in flux, and to 0.85 c_o 7.0 pore volumes after the change in flux. Reduction of the flux to 0.2 cm/hour resulted in a drastic reduction in lindane concentration of the effluent. After the passage of 3.4 pore volumes from the time of the reduction of flux, the lindane concentration of the effluent was reduced to only slightly higher than that obtained after the passage of 35 pore volumes of lindane solution during the initial flow at low flux. At low flux lindane was with-

held in the column in excess to that predicted by data from an equilibrium adsorption study. At high flux, lindane was held in the column to an extent less than that predicted by the adsorption data. Special determinations indicated that neither the OH^- concentration nor the Cl^- concentration of the effluent was high enough to indicate that decomposition of lindane had occurred in the column at low flux. The only plausible explanation for the disappearance of lindane at the low flux seems to be that the column acted as an extended filter and thus removed from the flow the coarser of the fine lindane particles contributing to lindane solubility in water.

Appendix IV

Summary Titles of Publications Pending

1. Concentration-temperature interactions of chlorinated hydrocarbons in water.
2. Adsorption of gamma-BHC from solutions on several selected adsorbents.
3. Adsorption of gamma and beta-BHC from solution: The differential heat of adsorption applied to adsorption from dilute solutions on organic and inorganic surfaces.
4. Adsorption of gamma and beta-BHC from solution: Adsorption isotherms and the solubility temperature effect.

CONCENTRATION-TEMPERATURE INTERACTIONS OF CHLORINATED HYDROCARBONS IN WATER

J. W. Biggar and R. L. Riggs

The importance of the solubilities in water of slightly soluble chlorinated hydrocarbons has not been adequately assessed or investigated. In fact, the interrelation between the solubilities and various adsorption-desorption reactions that occur during the movement and mixing of waters in streams and soils appears to be essential for better use and control of pesticides. Evidence is increasing to indicate that solubility may be a determining factor in the disappearance of many of these materials from soils.

Of no less importance - from a biological, as well as a physio-chemical point of view - is the significant effect that temperature has on the solubility and the adsorption-desorption reactions. The somewhat erratic behavior of the slightly soluble or poorly adsorbed pesticides in lakes, streams and drainage waters may be attributed to changes in temperature. Such changes require new equilibria to be established between suspended particulate matter solid phase or adsorbed pesticide and solutions. Seasonal changes of pesticide concentration in the region of bottom muds of lakes subject to turnover may also be subject to temperature changes.

A survey of the literature yielded no extensive satisfactory water solubility data for a number of the chlorinated hydrocarbons under investigation, particularly as the solubility is affected by temperature.

The most commonly used pesticide, DDT, has been the subject of most of the research conducted on chlorinated hydrocarbon pesticide solubilities in water. Richards and Cutkomp (1946) reported a solubility of from 0.2 to 1.0 ppb at 15°C, determined by bioassay with mosquito larvae. Gauvadan and Poussel (1947) estimated 100 ppb at 18°C by a nephelometric technique. Roeder and Weiant (1946) estimated the solubility of DDT in water to be 10 to 100 ppb at room temperature by observing nerve reactions in cockroaches. Using radiometric techniques, Babers (1955) reported solubility values of 5.9 ppb, 37 ppb and 45 ppb at temperatures of 2°C, 25°C and 37°C respectively. Sazonov (1956) determined the solubility of DDT to be less than 1.0 ppm. Bowman et al (1960) used C^{14} labeled DDT and ultracentrifugation to determine that the solubility is a function of the particle size allowed to remain in the solution. At a particle size of 41 Å, they determined the solubility of DDT in water to be 1.2 ppb. Biggar and Riggs (1967) reported a value of 1.7 ppb for DDT as determined by ultracentrifugation and analysis by electron capture gas chromatography. The solubility of lindane in water was determined by Slade (1945) to be 10 ppm. Hancock and Laws (1955) and

Ivanov (1956) reported values of 7.0 ppm and 8.0-8.5 ppm respectively. A solubility of 31.8 ppm was reported by Sazonov (1956).

Richardson and Miller (1960) determined the solubilities of several pesticides at various temperatures by means of UV spectrophotometry and, in the case of lindane, polarography.

Robeck et al. (1965) determined the solubility of five pesticides and one herbicide at 25°C and at particle sizes ranging from 0.04 μ to 5 μ.

A second factor prompted the need for solubility-temperature data. In studying the energetics of adsorption-desorption reactions in soils, the effect of temperature on the concentration is needed for the calculation of certain thermodynamic quantities. Such a need prompted an investigation of the temperature solubility interaction for the range of temperature encountered in the adsorption-desorption experiments.

The true solubility in water of many of these slightly soluble chlorinated hydrocarbons is difficult to ascertain because of their hydrophobic nature and the analytical problems associated with such low concentrations. The possibility that compounds with very few hydrophilic groups will concentrate at the air-water interface, has been shown to occur for many compounds (Davies, 1963). The presence of contaminants in small quantities may significantly change the solubility of extremely insoluble compounds. It has been pointed out previously that groups of molecules as well as individual species may exist (Bowman et al., 1960). Much effort was expended to disselve the compounds in such a way as to form individual molecular species. The concentration in solution and the effect of temperature on that concentration for particular equivalent diameter particle species are reported to emphasize both the possible particulate nature of the material and its changes with temperature.

Procedure

Samples of the chemicals, all greater than 99.9% purity, were added to a liter of distilled water (double distilled from glass) in excess concentration of 5 ppm. The samples were treated ultrasonically (Biggs and Biggar, 1965) and shaken for 2 weeks in a constant temperature bath at 15, 25, 35 and 45°C ± 0.05°C. They were filtered through a sintered glass filter of 4.5 - 5.5 μ porosity. Samples were centrifuged at the above temperatures for one-half hour at three velocities, which are expressed in terms of equivalent particle diameters - based on uniform spherical particles and the application of Stokes law. Aliquots of 100 and 200 ml were taken after centrifuging. The aliquots were combined (600-700 mls) and extracted three times with nanograde hexane (redistilled over Na) using 100;50;50 ml volumes. Extracts were combined, eluted through a column of anhydrous Na_2SO_4 and concentrated to 0.2-1.0 ml using Kuderna-Danish evaporative concentrators. Extraction and recovery efficiencies (99-100%) were determined by adding known amounts of pesticide before sampling. Calibration curves were prepapred for each pesticide in nanograde hexane. In some instances, aldrin was added as an internal standard.

One to five microliter aliquots of concentrate were chromatographed using a Varian Aerograph 600-B, employing a concentric 250 mc H^3 election capture detector operated at 90 V. Other GLC parameters were as follows: the columns employed were 5' x 1/8" pyrex; packed with 5% Dow 11, 5% DC 200, and 5% QF-1, on 60/80 Chromosorb W; the carrier gas was molecular sieve (13X) purified N_2 at a flow rate of 50 ml/min. Injector, column, and detector temperatures were 225, 180 and 200°C respectively. The chromatograms were recorded on a Honeywell-Brown Electronik 15 0-1 mV recorder equipped with a 201-B Disc integrator. Nemagon was analyzed using the following conditions: injector, oven and detector temperatures were 100, 90 and 100°C respectively; Column flow rate was 30 ml/min.

A Dohrman C-200 microcoulometer and T-300-S halide titration cell were also used for samples of high solubility, such as lindane.

Retention times and sensitivities for these systems have been generally noted (Bonelli et al.,1963; Burchfield & Johnson, 1965) and need not be listed here. Each solubility value reported represents the average of at least 3 determinations.

Results

Previous work on the dispersion of p,p'DDT in water indicated the difficulties and dangers of assuming completely uniform molecular distribution of the slightly soluble hydrocarbons. Despite the rigorous methods to obtain true solution of the materials investigated, it was still considered desirable to centrifuge them to constant concentration at two or three velocities. The results of the analyses are presented as the concentration for these three velocities expressed as equivalent particle size assuming Stokes law and the appropriate temperature and density of the solute and solvent.

Table I

In table I a summary is presented of the concentration of all compounds measured at 25°C. Some of the materials investigated did not exhibit a size distribution characteristic of the aldrin group although the TDE, DDE and o,p'DDT materials were not investigated in this regard. Aldrin, dieldrin and endrin, having somewhat similar molecular characteristics, behaved similarly with endrin proving to be the most soluble. In hexane both dieldrin and endrin are much less soluble than aldrin, the range being from 7 to 98 gm. per 100 ml, but considerably higher than in water as expected. It is quite evident from this limited table and other reports (Edwards, 1966) that the least soluble p,p'DDT is also the most persistent in the environment. The others more or less follow in the order of their solubility although this is not the only factor important in the degradation of these insecticides. In some cases lindane, the most soluble in the group with the exception of nemagon, has shown more persistence than aldrin although the latter is oxidized to dieldrin which is more persistent than lindane.

One of the physical factors of a constantly changing environment which can significantly affect the observed behavior of the pesticide is temperature. The temperature range in the present investigation covers a range commonly found in nature. Since it is not uncommon to use a filter of fine pore size to prepare samples prior to analysis, table II presents data for a number of materials expressing the concentration changes with temperature for equivalent particle size or filter size of 5μ. The material reported may be present in true solution or be subject to nonuniform distribution as previously noted.

TABLE II

In all cases investigated the temperature had a significant effect on the saturation concentration of the insecticides in water. Increases ranged from 2.5 fold for p,p'DDT to >9 fold for Methoxychlor. The changes in concentration in solution for some of the compounds are illustrated in figures 1 and 2. The wide differences in the

Figures 1+2

effect of temperature on the concentration is quite evident by comparing p,p'-DDT and Heptachlor epoxide. None of the compounds exhibited a linear change with temperature.

In figure 2 it is evident that the cyclodiene compounds related to aldrin respond similarly, there being a 6-fold change in the concentration over the 30°C temperature change.

TABLE III

In table III the changes in concentration at saturation with changes in equivalent particle diameter and temperature are given for some compounds. For the smallest size the change in concentration with temperature exceeds 10-fold for compounds such as aldrin and endrin while for p,p'DDT it barely exceeds a 2-fold change. In figure 2 these changes are given for the aldrin group for the largest and smallest equivalent particle diameter. It is apparent for these compounds that the changes of concentration are nonlinear both with respect to temperature and with respect to equivalent particle size within a given compound. In general the temperature effects on concentration show the 0.05μ size lying between the 0.01 and 5.0μ size.

The behavior of the compounds with respect to temperature as shown in figures 2 and 3 is indicative of what might be expected for the solubility of a compound in a solvent. For an ideal solution the relation between the mole fraction X_A of compound (A) in a solvent with respect to temperature is given as

$$\ln X_A = -\frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) \qquad (1)$$

Figures 1+2

where T_m is the melting point of the solid and ΔH_f the heat of fusion. The assumption of constant ΔH_f is required which implies no large differences between heat capacities of the reactants and products. If ΔH_f changes appreciably then additional terms must be added to equation (1).

The equation indicates that a lower temperature results in a lower solubility for a given solute, and the larger the heat of fusion the more rapidly the solubility will change with temperature. Although the existence of an ideal solution is not expected in the present systems, some idea of the departure may be had by plotting the mole fraction vs. 1/T. The results are presented for the aldrin group in figure 3 for the 5μ equivalent particle size.

Considering the difficulties experienced in preparing and analyzing the materials together with the restriction of ideality, the requirements of linearity are reasonably good.

Discussion and Conclusions

Although the solubility of each compound investigated cannot be stated absolutely, it is sufficiently clear that the compounds are very slightly soluble and their solubility changes significantly with temperature. Consequently an organism or plant might be subject to varying concentrations depending on the temperature of the environment. These concentrations may change as much as ten fold for a 30°C change in temperature. It is not surprising then that the amount of pesticide in solution in relation to particulate matter or in the absence of particulate matter may change as samples of water are withdrawn from drains, streams, lakes and other water bodies. Consequently, differences in adsorption and desorption of pesticides by soil and other materials may be controlled not only by the difficulty of solution in aqueous media but more significantly by variations in temperature. This problem together with ascertaining the importance of increasing concentration of the organic at the air-water interface deserve additional investigation.

Summary

The concentration of several chlorinated hydrocarbons in water at saturation has been measured with respect to changes in temperature and speed of centrifuging. The effect of the latter treatment is expressed in terms of the equivalent spherical particle diameter. A 2- to 10-fold change in concentration was measured for the compounds over a 30°C change in temperature. The effect of the temperature change on pesticide in solution in various bodies of water particularly in the presence of adsorbents was discussed.

Figure 1. Changes in concentration of aqueous solutions saturated with various pesticides as a function of temperature.

Figure 2. The effect of temperature on the concentration of aldrin, dieldrin and endrin in saturated aqueous solutions presented as two different equivalent particle diameters.

Figure 3. Changes in the mole fraction of selected pesticides in relation to the reciprocal of the absolute temperature for saturated aqueous solution and an equivalent particle size of five microns.

Literature Cited

Babers, F. H., J. Am. Chem. Soc. 77, 4666 (1955).

Biggar, J. W., Dutt, G. R., and Riggs, R. L., Bull. of Environ. Contam. Toxicol. 2, 90 (1967).

Bonelli, E. J., Hartman, H., and Dimick, K. P., J. Agr. Food Chem. 12, 333 (1964).

Bowman, M. C., Acree, F. Jr., and Corbett, M. K., J. Agr. Food Chem. 8, 406 (1960).

Burchfield, H. P. and Johnson, D. E., "Guide to Analysis of Pesticide Residues", U.S. Department of Health, Education and Welfare, Washington, D.C. (1965).

Davies, J. T., and Rideal, E. K., "Interfacial Phenomena", Academic Press, New York (1963).

Edwards, C. A., Residue Reviews 13, 83 (1966).

Gauvadan, P., and Poussel, H., Compt. Rend. 224, 683 (1947).

Hancock, W., and Laws, E. Q., Analyst 80, 665 (1955).

Ivanov, K. A., Gigiena i Sanit. 21, 82 (1956).

Richards, A. G., and Cutkomp, L. K., Biol. Bull. 90, 97 (1946).

Richardson, L. T., and Miller, D. M., Can. J. Botany 38, 163 (1960).

Riggs, R. L., and Biggar, J. W., Soil Sci. Soc. Amer. Proc. 29, 629 (1965).

Robeck, G. G., Dostal, K. A., Cohen, J. M., and Kreissal, J. F., J.A.W.W.A. 57, 181 (1965).

Roeder, K. D., and Weiant, E. A., Science 103, 304 (1946).

Sazonov, P. V., Bogdarina, A. A., and Gudkova A. S., Trudy Vsesoyuz
    Inst. Zashchity Rastenii 7, 128 (1936).

Slade, R. E., Chem. and Ind. 40, 314 (1945).

Table I

Concentration in water of selected chlorinated hydrocarbons expressed as an equivalent particle size in microns at 25°C. Concentration expressed in ppb.

	Particle Size (microns)		
	0.01	0.05	5.0
Lindane	150	600	6800
Aldrin	13	140	180
Dieldrin	22	150	195
Endrin	24	180	250
Heptachlor			180
Heptachlor epoxide			200
p,p'DDT	1.7	6	25
o,p'DDT			85
p,p'TDE (DDD)			90
p,p'-TDEE 1/			140
p,p'-DDE			120
o,p'-DDE 1/			140
Tech B-DDT 2/		17	40
Methoxychlor			45
Nemagon 3/			1150

1/ synthesized by dehydrohalogenating parent compounds.

2/ mixture of 76% p,p'DDT; 22% o,p'DDT, o,o'-DDT, p,p'-TDE; 2% p,p'-DDE.

3/ concentration in ppm. All others ppb.

Table II

Concentration of selected pesticides in water as a function of temperature for particle sizes less than 5μ equivalent diameter. Concentration expressed in ppb.

	Temperature °C			
	15	25	35	45
Lindane	2150	6800	11,400	15,200
Aldrin	105	180	350	600
Dieldrin	90	195	400	650
Endrin	130	250	420	625
Heptachlor	100	180	315	490
Heptachlor epoxide	110	200	350	600
p,p'DDT	17	25	37	45
o,p'DDT	50	85	135	200
p,p'TDE (DDD)	50	90	150	240
o,p'TDE DDD	60	100	280	315
p,p'TDEE 1/	65	140	260	310
p,p'DDE	55	120	235	450
o,p'-DDE 1/		140		
Methoxychlor	20	45	95	185

1/ synthesized by dehydrohalogenating the parent compound.

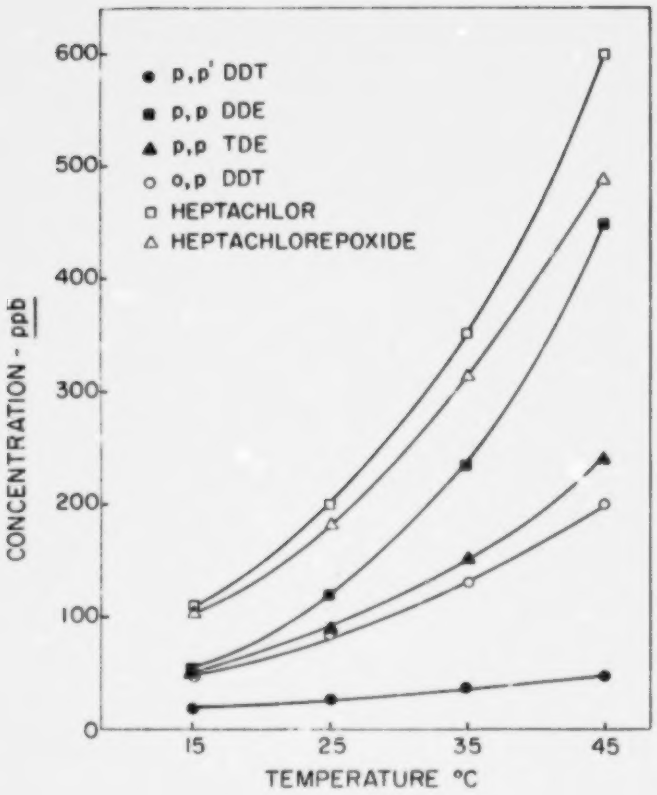
Table III

Concentration of selected hydrocarbons in water at four temperatures and three equivalent particle diameters.

	Equivalent Particle Size µ	Temperature °C 15	25	35	45
Lindane	0.01	75	150	315	575
	0.05	330	600	950	1450
	5.0	2150	6800	11,400	15,200
Aldrin	0.01	5.5	13.5	30	65
	0.05	52	140	235	455
	5.0	105	180	350	600
Dieldrin	0.01	10	22	47	90
	0.05	65	150	270	480
	5.0	90	195	400	650
Endrin	0.01	10	24.5	58	120
	0.05	90	180	315	518
	5.0	130	250	420	625
p,p'DDT	0.01	-	1.7	2.6	3.9
	0.05	2.5	6	13	27.5
	5.0	17	25	37	45

Acknowledgement

This research was supported by grant WP-0008 from the National Institute of Health, U. S. Public Health Service, Department of Health, Education and Welfare.


● p,p' DDT
■ p,p DDE
▲ p,p TDE
○ o,p DDT
□ HEPTACHLOR
△ HEPTACHLOREPOXIDE
600
500
400
300
200
100
0
CONCENTRATION - ppb
15
25
35
45
TEMPERATURE °C

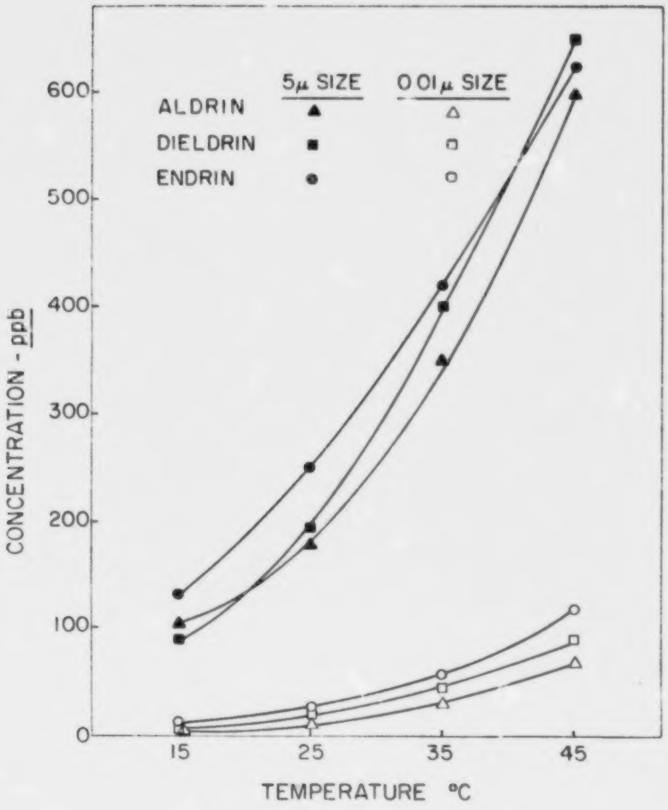
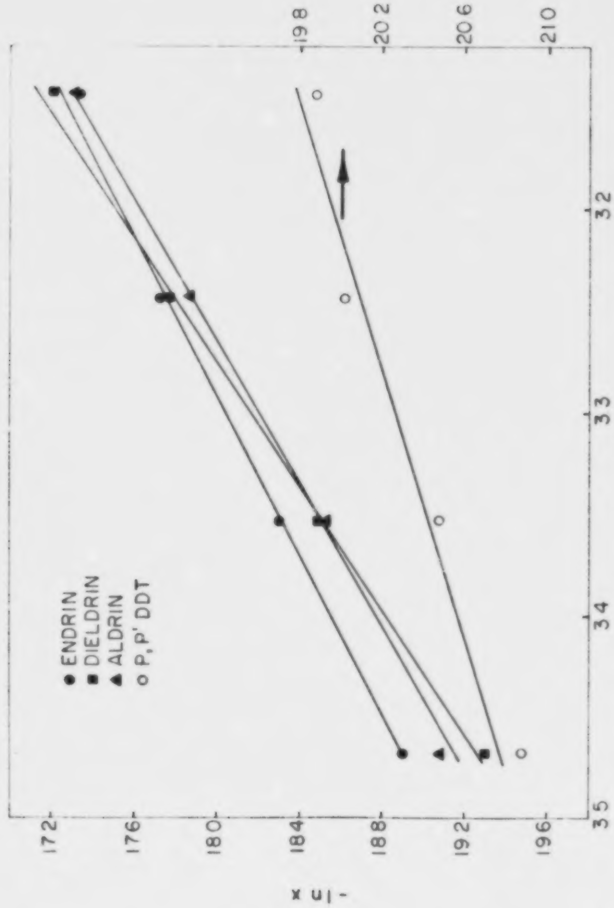

5μ SIZE
0.01μ SIZE
ALDRIN ▲ △
DIELDRIN ■ □
ENDRIN ● ○
CONCENTRATION - ppb
0
100
200
300
400
500
600
15
25
35
45
TEMPERATURE °C

Fig 2



● ENDRIN
■ DIELDRIN
▲ ALDRIN
○ P, P' DDT
- ln x
172
176
180
184
188
192
196
198
202
206
210
35
34
33
32
$\frac{1}{T} \times 10^3$

Fig 3

Adsorption of Gamma-BHC from solutions on several selected adsorbents

by

A. C. Mills and J. W. Biggar[1]

Department of Water Science and Engineering

University of California, Davis, California 95616

Abstract

The adsorptive behavior of gamma-BHC from water, alcohol, benzene and hexane on to several selected adsorbents has been investigated at 20°C. Both liquid scintillation counting and electron capture gas chromatography were utilised in the procedure to assess any decomposition or isomerization that may occur during the adsorption. In general the extent of adsorption from the solvents increased in the order ethanol < benzene < hexane ≪ water. Relatively low adsorption from hexane and benzene occurred on peaty muck, with the greatest adsorption on silicagel and Venado clay. No significant adsorption occurred from ethanol except on peaty muck. The importance of dipole-dipole interactions in gamma-BHC adsorption was deduced. Although no decomposition occurred in aqueous and alcohol solvents, some was observed in benzene and hexane solvents. Solubility and other solvent differences markedly influence the uptake of pesticide by the different surfaces.

---

[1] Investigation supported by Training Grant 5T1-WP-7 and Research Grant WP-0008 from the Federal Water Pollution Control Administration and is part of a Ph.D. thesis by the senior author. The senior author is presently at C-52 N.D. South, I AFPRO, Extension II, New Delhi 16, India.

The importance to Public Health of determining the behavior of pesticide in soils has been expressed frequently in recent times. Because of the mobility of the pesticide brought about by the movement of water from land surfaces to water bodies, the inherent dangers of widespread dissipation of the chemical are increased. As an integral part of the movement process, the adsorption of the chemical is often an important step. This in turn is affected by the solvent, the surface of the solid and the nature of the chemical.

The insecticide lindane (99-100% γ-BHC) was chosen for the present study because it has been shown to be relatively persistent in soils (Edwards, 1966) and because it presents certain health hazards to man and animals through uptake by crops (Odumanova-Dunaeva and Kozlova, 1965). Of equal importance is its presence in various surface and groundwater supplies (Faust and Suffet, 1966).

Relatively few controlled laboratory experiments aimed at elucidating the adsorptive behavior of lindane on soils and related adsorbents have been reported. Lichtenstein (1958) measured the movement of lindane from one soil layer downward through lower layers of soil, initially containing no lindane, in cardboard cartons under various leaching regimes. Under leaching conditions lindane was determined to have moved the most in Plainfield sand and least in a muck soil. Where no water was applied lindane was found to have moved to the greatest extent in the muck soil, and not at all in the sand. Press (1959) applied lindane in isohexane to columns of different African soils. After measuring the different volumes of the solvent required to elute essentially all the lindane, he concluded that the finely particulate soils were relatively more adsorptive. Swanson, Thorp and Friend (1954) studied adsorption in a similar manner. Lindane was applied to soil columns in petroleum ether and leached with five aliquots of the solvent weighing the equivalent of the weight of the soil used. Exchange resins were found to hold no lindane, and the presence of organic matter seemed to have little effect in increasing lindane adsorption. The amount of lindane adsorbed, however, was closely correlated to percent clay content of the soil. One might expect that had aqueous solutions of lindane been employed by these workers, the adsorptive capacity of the organic fraction might have been found to be significant. Nose, Suzuki, and Fukunaga (1964) in their study of the adsorption of pentachlorophenol (PCP) from aqueous solutions concluded that organic matter is important for PCP adsorption in soil.

The aim of the present study was to ascertain by employing sensitive methods of analysis the nature of adsorption and decomposition of γ-BHC from solutions of very low concentrations such as can be encountered in the field. Several solvents, including water, and several adsorbents were employed in equilibrium adsorption studies. Another goal of this study was to ascertain whether the solvents with differing properties would measurably influence the adsorption in view of the fact that different carriers are often used in preparations.

Gamma-BHC is one of the isomers of the compound 1,2,3,4,5,6-hexachlorocyclohexane. The molecule is not planar, but the carbon ring assumes a puckered 'chair' form. In the gamma-isomer three chlorine atoms are equatorial (extending out roughly from what may be considered the plane of the ring) and three chlorine atoms are axial (projecting above or below the ring). In the beta-isomer all the chlorine atoms are equatorial. Lind, Hobbs, and Gross[4] note that since the β-isomer is concluded to be centrosymmetric one would expect the electric moment to be zero. They determined a dipole moment for β-BHC which they consider indistinguishable from zero within experimental error, while they measured a dipole moment for γ-BHC in benzene at 30°C of 2.84 debye units.

Experimental Materials and Methods

Materials

Untagged crystalline γ-BHC obtained from the supplier was certified to be 99-100% gamma-isomer. β-BHC had guaranteed purity of 95%. The radioactive gamma-isomer was obtained as C^{14} uniform-labeled compound supplied in benzene solutions. The radiochemical purity was determined by the supplier to be 98% or higher by thin-layer chromatography.

The solvents employed were obtained from several suppliers. Benzene was reagent grade, A.C.S., having a thiophene content of 0.001%. Hexane was nanograde hexane and consisted of a mixture of isomers with the formula C_6H_{14}. Ethanol was obtained as 200-proof ethyl alcohol.

Several adsorbents, including soils, clays, exchange resins, silica gel, and alumina, were utilized for the adsorption studies. The exchange resins employed were 100-200 mesh Dowex 50W-X8 (H^+ form) and 100-200 mesh Dowex 1-X8 (Cl^- form). Silica gel (100-200 mesh) certified reagent was obtained as a Fisher certified reagent. Fisher-certified neutral alumina (pH 8.15) with a size range of 80-200 mesh was employed, as well as a basic alumina (pH 10.0) of the same size range. Magnesium hydroxide was prepared by the authors by combining aqueous solutions of reagent grade NaOH and $MgCl_2$.

Homoionic samples of Wyoming bentonite and kaolinite were prepared in the laboratory by leaching and sedimentation. The samples of Ca- and Na-bentonite and Ca-kaolinite were of the particle size range 0.2 to 1.0 micron.

Venado clay was determined by X-ray diffraction analysis to contain approximately 40% montmorillonite. All the soil samples were prepared by saturating with solutions of Ca acetate or Mg acetate, leaching with distilled water and drying. Then they were ground to less than 1.0 mm sieve size with a porcelain mortar and pestle, and oven-dried on aluminum foil at 110°C for 24 hours.

Table 1 shows the results of carbon and surface area determinations made by the authors on a few of the adsorbents. Percent carbon content was determined by total combustion in a combustion train (as described in *Methods of Soil Analysis*, No. 9 in the Agronomy Series, p. 1367, American Society of Agronomy, Inc., Madison, Wisconsin, 1965). Surface areas were determined according to the ethylene glycol method described by Bower and Gschwend (1952). Hydrogen peroxide treatment was performed on separate samples of Venado clay to reduce the organic matter content.

Table 1. Some characteristics of selected adsorbents.

Adsorbent	pH	Cation exchange capacity me/100 gm	Percent carbon (of oven-dry weight)	Total surface area m^2/gm
Ca-Staten peaty muck	6.6	54	11.9	2.3×10^2
Ca-Venado clay	8.5	48	3.1	4.2×10^2
H_2O_2-treated Ca-Venado clay	*	*	1.2	4.1×10^2
Ca-Columbia silt loam	7.5	14	1.1	*
Ca-bentonite	8.3	80	0.08	8.1×10^2
Silica gel	4.4	*	*	8.9×10^2

* Undetermined.

The surface area of silica gel appears to be excessively high compared to reported values of .710 ± 60 m^2/gm (Dyne and Sagert 1966) calculated by the B.E.T. equation using N_2 as the adsorbent. However, the present silica gel had a particle size of 100-200 mesh compared to 30-60 mesh used by the cited investigators. Consequently 890 m^2/gm may not be an unreasonable value. The surface area reported for Ca-bentonite compares closely with those obtained by Bower and Gschwend (1952).

Applying a factor of 1.9 (ratio of the weight of total organic matter to the weight of carbon) to the percent carbon obtained for Staten peaty muck, the organic matter content of this soil is 22.7%. A comparison of values for the percent carbon in the case of untreated and H_2O_2-treated. Venado clay shows that the H_2O_2 treatment removed a little less than two-thirds of the organic matter present in this soil.

Methods

All solutions were prepared with a constant concentration of radiochemical (5.0 μc/liter) with the remainder made up with the normal non-radioactive isomer. Five grams of oven-dried adsorbent were weighed into a 125-ml glass-stoppered Erlenmeyer flask. (Ten grams of adsorbent were employed for some of the materials as indicated.) To ensure low, uniform moisture content of the adsorbents, in most cases the flasks were placed in an oven for 36 hours at 110°C, before the addition of organic solutions, and 15 hours at 60°C before the addition of aqueous solutions. Following the heat treatment, 25 ml of the appropriate solution were added by pipette to each flask. Duplicates were included for each concentration level and each adsorbent. Adsorbent blanks and standard blanks in duplicate were also included. The flasks were stoppered, covered with polyethylene bags, and placed in a constant-temperature AMINCO water bath which was set at the desired temperature. (Temperature variation in the bath did not exceed 0.05°C.) The flasks were shaken in the bath at a moderate rate for a period of 20 hours. Following an additional 50 hours during which time the flasks remained at rest, sampling was performed. Time studies indicated that for all the systems employed adsorption equilibrium was achieved by the end of this period.

Aliquots of the equilibrium solution were removed directly from the flasks, in place in the bath, in the case of systems having benzene or hexane as the solvent. For the ethanol-containing systems and aqueous systems, the flasks were removed from the bath, swirled, and then the contents poured into 50-ml stainless steel centrifuge tubes. These were immediately centrifuged at the temperature of the water bath (± 0.8°C) for 20 minutes at 10,000 rpm. This procedure ensured sedimentation of the clay in the ethanol and aqueous media. Ten ml of the supernatant were transferred to a glass-stoppered test tube. The aqueous solutions were extracted by adding 10 ml of nanograde hexane above the aqueous solution and inverting the stoppered test tube back and forth for 1½ minutes. Longer mixing times did not improve extraction.

Analysis of the equilibrium solutions was performed both by liquid scintillation counting (L.S.) in a Packard Tri-Carb liquid scintillation spectrometer and by electron-capture gas chromatography (G.C.) with an Aerograph Hy-Fi, Model 600-B gas chromatograph. The Honeywell recorder used in conjunction with the gas chromatograph was equipped with a disc integrator. The purpose of employing dual forms of analysis was to determine whether or not decomposition of the BHC isomer had occurred in the adsorption flasks, and, if so, the extent of decomposition. When decomposition was concluded to be nil (concentration of the equilibrium solution by G.C. at least 90% or more than the concentration determined by L.S. analysis), the L.S. equilibrium concentration values were the values used for calculation of the amounts adsorbed. Precision accuracy of the G.C. analyses was concluded to be only about one-half of that of the L.S. analyses.

Solubilities of γ-BHC in aqueous medium at 20°C and 30°C were determined by the authors. To correspond to the aqueous systems used in the adsorption experiments the solutions contained 0.5% ethanol by volume. In addition, the solubility of γ-BHC in nanograde hexane was determined at 10°C and 20°C. Aliquots removed for analysis from the saturated solutions were filtered through a 4 - 6 micron fritted glass filter. Analysis was performed, following appropriate dilutions, by gas chromatography. Table 2 shows the results of the solubility determinations.

Table 2. Solubility of γ-BHC in aqueous and hexane solutions at 10, 20 or 30°C.

Isomer	Solvent	Temperature (°C)	Concentration of Saturated Solution
γ-	Distilled water with 0.5% ethanol	20	8.5 μg/ml
		30	13.1 μg/ml
γ-	Nanograde hexane	10	9.8 mg/ml
		20	14.0 mg/ml

Results and Discussion

The influence of heat pre-treatment of soil upon subsequent adsorption of lindane from benzene solutions was demonstrated by an experiment using Ca-Venado clay as adsorbent. Table 3 indicates the results obtained when varying the temperature during 72-hour heat treatments of 10 grams of the soil prior to the addition of a benzene solution containing 5 μg/ml γ-BHC. It is apparent that positive adsorption of γ-BHC from benzene solutions onto Venado clay is possible only if the adsorbent has been preheated above room temperature. The reason for this may be linked to the loss of interlayer water at higher temperatures. This water may be adsorbed on sites which have more affinity for the γ-BHC molecules than for benzene molecules.

Table 3. Effect of Heat Pre-treatment of Ca-Venado Clay Upon Adsorption of γ-BHC from Benzene Solution at 25°C.

Temp. of Pre-treatment (°C)	Equilibrium Conc. (μg/ml)	% Deviation between duplicates	x/m (μg adsorbed per gm of adsorbent)
25	5.05	0.2	0.12
111	4.60	0.5	1.00
224	4.49	0.8	1.27

The influence of the cation on the exchange complex and of soil organic matter upon adsorption of γ-BHC on Venado clay from a 5.0 μg/ml aqueous solution was indicated in another experiment. Solution volume added in this case was 20 ml. The results are shown in table 4. It is apparent from

Table 4. Effect of Saturating Cation and H_2O_2-Treatment upon Adsorption of γ-BHC on Ca-Venado Clay from a 5 μg/ml Aqueous Solution at 20°C.

Adsorbent	Equilibrium Conc. (μg/ml)	% Deviation Between Duplicates	x/m (μg/gm)
Ca-Venado clay	0.373	0.2	18.5
Mg-Venado clay	0.372	0.1	18.5
Ca-Venado clay (H_2O_2-treated)	0.745	0.2	17.0

these data that changing the saturating cation from Ca^{++} to Mg^{++} has no apparent effect upon adsorption from aqueous solutions. On the other hand, a definite reduction of the x/m value is effected by the H_2O_2-treatment of Venado clay. This reduction is undoubtedly due to the partial loss of organic matter. Table 1 showed that the H_2O_2-treated Venado clay still contained 1.2% carbon, slightly more than one-third of the carbon content of the untreated soil. We have noted that Venado clay contains approximately 40% montmorillonite. The x/m value for the adsorption of γ-BHC on Ca-bentonite from a 5.0 μg/ml aqueous solution is of the order of 10 μg/gm, as shown in table 8. Consequently, comparing 10 to 17 μg/gm, one must conclude that adsorption of γ-BHC from aqueous solutions is influenced considerably by that portion of the organic matter which is quite resistant to the H_2O_2-treatment and which is probably, in effect, adsorbed strongly on the clay surface.

A summary of the results of experiments on adsorption of γ-BHC at 20°C from solutions of a single concentration in benzene, hexane, ethanol, and water is given in tables 5, 6, 7, and 8, respectively. The results for the adsorbents are arranged in each case in the order of increasing x/m values. Negative values in the table arise in part from differential evaporation losses and exclusion of the adsorbate relative to solvent uptake by the adsorbent.

Table 5

Adsorption of γ-BHC from 100 μg/ml benzene solution

Adsorbent	x/m (μg/gm)
Na-montronite	-2.3
Ca-bentonite*	-2.2
Na-bentonite	-1.9
Cation exch. resin	-1.6
Anion exch. resin	-1.6
Na-kaolinite	-1.3
Ca-Staten peaty muck*	-1.2
Alumina (basic)*	2.7
Ca-Columbia silt loam*	2.8
$Mg(OH)_2$	6.4
Ca-Venado clay*	12.1
Silica gel*	13.5

Table 6

Adsorption of γ-BHC from 100 μg/ml nanograde hexane solution

Adsorbent	x/m (μg/gm)
Cation exch. resin	-1.8
Anion exch. resin	1.4
Ca-Staten peaty muck*	38.8
Na-kaolinite	50.7
$Mg(OH)_2$	66.4
Alumina (neutral)	68.6
Na-bentonite	72.5
Alumina (basic)*	80.6
Ca-Columbia silt loam*	94.1
Ca-bentonite*	97.2
Ca-Venado clay*	166.0
Silica gel*	245.0

* 10.0 grams rather than 5.0 grams of adsorbent employed

Table 7

Adsorption of γ-BHC from 5.0 μg/ml ethanol solution

Adsorbent	x/m (μg/gm)
Silica gel	-1.10
Ca-bentonite	-0.60
Ca-Venado clay	-0.30
Ca-kaolinite	0.15
Ca-Columbia silt loam	0.35
Ca-Staten peaty muck	3.70

Table 8

Adsorption of γ-BHC from 5.0 μg/ml aqueous solution

Adsorbent	x/m (μg/gm)
Ca-kaolinite	2.70
Ca-Oakley sand	9.40
Silica gel	9.70
Ca-bentonite	10.3
Ca-Columbia silt loam	16.3
Anion Exch. resin	20.6
Ca-Venado clay	22.5
Cation exch. resin	24.6
Ca-Staten peaty muck	24.6

The adsorption differences of γ-BHC from the different solvents may be assumed to be due in part to the differing solubilities of γ-BHC in them, and, in part, to the structure and affinity of the solvent molecule for the particular adsorbent. It is apparent, first of all, making allowance for the differences in initial concentration, that lindane most effectively competes for adsorption sites with water, and is least effective when competing with ethanol. To generalize for the adsorbents employed, we may say that the adsorption of γ-BHC from the solvents increases in the following order: ethanol < benzene < hexane < water. With the exception of the position of ethanol, the other three solvents are arranged in the order of decreasing solubility of γ-BHC. One can hypothesize, then that the combination of ethanol's polarity plus its organophilic character is important in making it most effective in competing with γ-BHC for adsorption sites.

With a few exceptions the order of adsorbents shown in table 5 is the same as that in table 6. Since the solubility of γ-BHC in benzene is about 14 times that in nanograde hexane, it is understandable why lower x/m values were obtained for the benzene system. But, in addition, the competitive effectiveness of the benzene molecule may be greater than that of hexane due to the differing molecular shape and electrical properties. The benzene molecule is more "compact" than hexane, possibly improving adsorption in spaces between the exchangeable ions on the oxygen surfaces of the kaolinite. Also the cross sectional area of benzene corresponds closely with that of lindane although the benzene molecule is planar in contrast to the lindane molecule. Thus lindane has little advantage over benzene in terms of size and shape while it is more compact than hexane.

Judging by the relatively high adsorption of γ-BHC on silica gel, clays and alumina particularly with respect to hexane in comparison to Staten peaty muck, it would seem the polarity of lindane may be important in its adsorption on polar inorganic surfaces.

Table 7 indicates that there is no significant adsorption of γ-BHC from ethanol except on Ca-Staten peaty muck. This gives us another indication that the polar character of this compound is important in its adsorption on silica gel, clay minerals, and Venado clay. Apparently the strong polar nature of ethanol together with its tendency to form hydrogen bonds allows it to compete effectively against γ-BHC on these adsorbents. The positive adsorption of the compound from ethanol on Staten peaty muck leads one to conclude that the non-polar organic constituents of this soil may have more affinity for lindane than for ethanol.

Referring to table 8, the order of adsorption from water has been changed considerably compared to the benzene or hexane systems. The exchange resins and the muck, as well as Venado clay, exhibit the highest affinity for γ-BHC. It is apparent that water molecules would not be attracted to the non-polar organic constituents which make up the matrix of the exchange resins as well as a considerable part of the muck soil. So, with such solvent competition eliminated it is understandable why the highest x/m values were obtained for these materials. This should also explain why a significantly higher degree of adsorption occurred on Ca-Venado clay compared to Ca-bentonite.

The fact that the water molecule as a dipole can offer some competition for adsorption sites on crystal surfaces of clays, silica gel, and sand accounts for the lower adsorption values for γ-BHC on these adsorbents relative to the organic-type (or organic matter-containing) adsorbents. Although the dipole moment of water is less than that for γ-BHC (1.84 compared to 2.84 debye units for γ-BHC), water tends to form hydrogen bonds with crystal surfaces. And it is likely that the type of hydrogen bond formed by water (O-H-------O) with oxygen surfaces is of greater energy than that possibly formed by γ-BHC (C-H-------O). This is because of the greater polarity of the O-H group compared to C-H. (The C-H bond moment has been estimated as 0.4D and that for O-H has been calculated as 1.52D, Barrow, 1961).

We may compare the adsorption values for γ-BHC from water on Ca-kaolinite and Ca-bentonite in terms of total specific surface area rather than the mass of clay. On this basis the adsorption on Ca-kaolinite far exceeds that on Ca-bentonite--0.18 $\mu g/m^2$ vs. 0.0127 $\mu g/m^2$. Assuming that interlayer adsorption of γ-BHC on bentonite does occur, it would appear that this molecule can compete with the water molecule much more effectively on the hydroxyl surfaces of kaolinite than on the oxygen surfaces of bentonite.

The importance of dipole-dipole interactions in the adsorption of γ-BHC from solution has been indicated by the above data. Dispersion forces may also be important. According to an equation given by Verwey and Overbeek (1948) the energy of adsorption due to dispersion forces is a function of the distance from the center of the adsorbed particle to the clay surface, the polarizabilities of the clay ions and the adsorbed molecule, and the ionization potentials of the clay ions and the adsorbed molecule. Values for the ionization potentials were not available. But the polarizabilities of γ-BHC and of each of the four solvents were calculated using published values for refraction indices. On the basis of the calculated polarizabilities alone one would expect adsorption of γ-BHC on crystalline surfaces from the following solvents to increase according to the scheme: hexane < benzene < ethanol < water. But the true order with respect to the organic solvents is reversed. One can only conclude that given the limited information about the solvents and adsorbate used, the contribution to adsorption of dispersion forces may be important, but is unclear.

In the initial studies decomposition of γ-BHC was concluded to occur on certain adsorbents in hexane and in benzene, while very little or no decomposition occurred in the ethanol and aqueous systems. This was evident when G.L.C. analysis was compared with liquid scintillation analysis. Whenever decomposition was evident the G.L.C. analysis was used in calculation of the amount adsorbed such as appears in tables 5 and 6. This insured that decomposition products would not be considered as lindane adsorption although it cannot be concluded that these products would not interfere with lindane adsorption.

A general positive relationship between the pH of an adsorbent in distilled water and the extent of decomposition of γ-BHC in hexane or benzene solutions is indicated in table 9 although several inconsistencies are evident. For example, in benzene solution the clays are out of place. For hexane the alumina and Ca-Venado clay are reversed suggesting that such a relationship between pH as measured in aqueous solvents and decomposition in organic solvents may have limited value.

Table 9. Decomposition of γ-BHC in Benzene and Hexane at 20°C.

Adsorbent	pH (measured in distilled water)	Amount of γ-BHC Decomposed (μg.)	
		In Benzene solution**	In Hexane solution**
Silica gel	4.4	145	0
Ca-Staten peaty muck	6.6	169	0
Ca-Columbia silt loam	7.5	234	0
Ca-bentonite	8.3	96	0
Ca-Venado clay	8.5	166	165
Alumina (neutral)	8.15	-	2150
Alumina (basic)	10.0	2450	1690

Adsorption of gamma and beta-BHC from solution: The differential heat of adsorption applied to adsorption from dilute solutions on organic and inorganic surfaces.

A. C. Mills and J. W. Biggar
Department of Water Science and Engineering
University of California, Davis.

Abstract

Isosteric heats and heats of adsorption for constant change of interfacial tension were obtained for the adsorption of 1, 2, 3, 4, 5, 6, hexachlorocyclohexane on inorganic and organic materials. The latter quantity, $\Delta\bar{H}_{\phi}$, was shown to represent the true difference at equilibrium between the partial molar enthalpy of the adsorbed solute and that of the solute in solution. Values of $\Delta\bar{H}_{\phi}$ were calculated from the equation

$$\Delta\bar{H}_{\phi} = \frac{RT_1T_2}{T_2-T_1} \ln \frac{\left(m_2{}^s/m_2\right)_{T_2}}{\left(m_2{}^s/m_2\right)_{T_1}}$$

derived for dilute solutions assuming Henry's law applies and the properties of the surface remain unchanged by adsorption. From changes in $\Delta\bar{H}_{\phi}$ it was possible to conclude that a wide range of site energies occur on the inorganic surfaces studied, but a relatively narrow range of site energies

occurs on the organic fractions of the adsorbents for the range of surface coverage studied. Both the partial molar enthalpy $\Delta\bar{H}'$ and entropy $\Delta\bar{S}'$ corrected for the temperature-solubility effect of the solute were obtained. Values of $\Delta\bar{S}'$ increased uniformly with surface coverage which is to be expected if there is a range of energy sites and the degrees of freedom increase with surface coverage. It appears that the configurational entropy of β-BHC adsorbed from water on bentonite is quite high while the lowest $\Delta\bar{S}'$ values were obtained for γ-BHC and β-BHC adsorption from water on silica gel.

Introduction

In the course of studying the behavior of the gamma and beta isomers of 1, 2, 3, 4, 5, 6, hexachlorocyclohexane in soil materials, the differential heats of adsorption were found to be useful in describing differences in behavior because of the molecular properties of the two isomers and the organic-inorganic nature of the adsorbents. The chemical named is a common pesticide, moderately persistent in the environment. The soil materials studied include Wyoming bentonite, Staten peaty muck, Venado clay containing approximately 40 per cent montmorillonite and a small amount of organic matter, all calcium saturated, and silica gel. The differential heats of adsorption to be discussed in this paper were calculated from isotherm measurements of the adsorption from aqueous and hexane solvents. Isotherms were measured by using C^{14} tagged BHC and analyzing the equilibrium solutions both by liquid scintillation and gas-liquid chromatography. Surface coverages of maximum adsorption were estimated to be less than 0.1%. Additional details of the procedures are given elsewhere (1).

The isosteric heat of adsorption is defined as the differential heat of adsorption when the amount of adsorbate adsorbed is kept constant. It is calculated, for adsorption from solution, by means of an equation analogous to the Clausius-Clapeyron equation (2),

$$Q_{\Gamma} = - \frac{RT_1T_2}{T_2-T_1} \ln(a_{T_2}/a_{T_1})_{\Gamma} \quad , \qquad (1)$$

where a_{T_2} and a_{T_1} are the equilibrium activities of the solute in the bulk phase at absolute temperatures T_2 and T_1 at constant surface coverage (Γ). Then, values of Q_{Γ} may be plotted against values of x/m to show the way in which Q_{Γ} varies with the extent of coverage. Hill (3) has clearly pointed out, however, that for the adsorption of vapor, Q_{Γ}, the isosteric heat, does not represent the true difference in partial molar enthalpy of the adsorbate between the adsorbed and bulk phases. In his development he shows that Q_{Γ} equals $\Delta\bar{H}$ plus another term which includes the partial derivative $(\partial\sigma/\partial T)_{\Gamma}$, where σ is the two-dimensional spreading pressure. σ is defined as $\sigma = \sigma_s - \sigma$, where σ_s is the surface tension of the clean surface, and σ the interfacial tension produced by the monolayer at equilibrium. It is not easy to determine the values of $(\partial\sigma/\partial T)_{\Gamma}$, so that the true differential enthalpy change, $\Delta\bar{H}$, can be determined. But he has been able to derive another equation of the Clausius-Clapeyron type which yields the values of $\Delta\bar{H}$ directly. His equation is the following:

$$\left(\frac{\partial \ln p}{\partial T}\right)_{\sigma} = - \frac{\Delta\bar{H}}{RT^2} \quad . \qquad (2)$$

These heats are found by plotting values of σ (obtained from a form of the Gibbs adsorption equation) versus p for two temperatures from which values for p are taken for constant values of σ. In what follows the authors wish to derive an equation applicable to adsorption from dilute solutions which would be analogous to equation (2). As does Hill, we will assume that the solid surface is essentially inert--its thermodynamic properties are not changed by the presence or absence of adsorbate molecules. We will define c_2 as the concentration of solute in the bulk phase in µg/ml of solvent, and c_2^s as the concentration of solute in the adsorbed phase in µg/ml of adsorbed solvent.

At equilibrium the fugacities of the solute in the bulk and adsorbed phases are equal.

$$f_2 = f_2^s$$

and so

$$\ln f_2 + \ln f_2^s ,$$

where f_2 and f_2^s are the fugacities of the solute in the bulk phase and in the adsorbed phase, respectively. Let us consider the following functional relationships for $\ln f_2$ and $\ln f_2^s$:

$$\ln f_2 = g(T,P,c_2)$$

and

$$\ln f_2^s = h(T,P,c_2^s,\sigma),$$

where σ is the two-dimensional spreading pressure at the solid-solution interface, T is the absolute temperature, and P is the pressure. Then it follows that

$$d(\ln f_2) = \left(\frac{\partial \ln f_2}{\partial T}\right)_{P,c} dT + \left(\frac{\partial \ln f_2}{\partial P}\right)_{T,c} dP + \left(\frac{\partial \ln f_2}{\partial c_2}\right)_{T,P} dc_2 \qquad (3)$$

$$d(\ln f_2^s) = \left(\frac{\partial \ln f_2^s}{\partial T}\right)_{P,c_2^s,\sigma} dT + \left(\frac{\partial \ln f_2^s}{\partial P}\right)_{T,c_2^s,\sigma} dP + \left(\frac{\partial \ln f_2^s}{\partial c_2^s}\right)_{T,P,\sigma} dc_2^s + \left(\frac{\partial \ln f_2^s}{\partial \sigma}\right)_{T,P,c_2^s} d\sigma \quad (4)$$

Now, as shown by Klotz (4) for solution thermodynamics

$$\left(\frac{\partial \ln f_2}{\partial T}\right)_{P,c_2} = \frac{\bar{H}_2^* - \bar{H}_2}{RT^2} \quad (5)$$

and, so also

$$\left(\frac{\partial \ln f_2^s}{\partial T}\right)_{P,c_2^s,\sigma} = \frac{\bar{H}_2^* - \bar{H}_2^s}{RT^2} \quad (6)$$

where $\bar{H}_2^*$ is the partial molar heat content of the solute at zero pressure, $\bar{H}_2$ is the partial molar heat content of the solute in the bulk solution, and $\bar{H}_2^s$ is the partial molar heat content of the solute in the adsorbed phase. At very dilute concentrations we assume that Henry's law applies to the bulk solution

$$f_2 = kc_2.$$

Therefore,

$$\ln f_2 = \ln c_2 + \ln k \ ,$$

and upon differentiation

$$d(\ln f_2) = d(\ln c_2).$$

Thus,

$$\left(\frac{\partial \ln f_2}{\partial c_2}\right)_{T,P} = \left(\frac{\partial \ln c_2}{\partial c_2}\right)_{T,P} = \frac{1}{c_2} \ .$$

Then,

$$\left(\frac{\partial \ln f_2}{\partial c_2}\right)_{T,P} dc_2 = \frac{dc_2}{c_2} = d(\ln c_2).$$

We have defined c_2 such that

$$c_2 = (m_2/m_1)\rho_1 \ ,$$

where m_2 is the mass of solute in μg in the bulk solution, m_1 is the mass of solvent in grams in the bulk solution, and ρ_1 is the density of the solvent in the bulk solution at the mean temperature (of the two experimental temperatures, T_2 and T_1, which will appear in equation (11)). Then,

$$\ln c_2 = \ln m_2 - \ln m_1 + \ln \rho_1$$

and

$$d(\ln c_2) = d(\ln m_2) - d(\ln m_1) \quad .$$

Thus,

$$\left(\frac{\partial \ln f_2}{\partial c_2}\right)_{T,P} dc_2 = d(\ln m_2) - d(\ln m_1) = \frac{dm_2}{m_2} - \frac{dm_1}{m_1} \quad . \qquad (7)$$

In an entirely similar fashion we may treat the adsorbed phase, in which case we assume that

$$f_2^s = k'c_2^s$$

and, thus

$$d(\ln f_2^s) = d(\ln c_2^s).$$

Consequently,

$$\left(\frac{\partial \ln f_2^s}{\partial c_2^s}\right)_{T,P,\sigma} = \frac{1}{c_2^s}$$

and

$$\left(\frac{\partial \ln f_2^s}{\partial c_2^s}\right)_{T,P,\sigma} dc_2^s = d(\ln c_2^s) \ .$$

Further, we defined c_2^s such that

$$c_2^s = (m_2^s/m_1^s)\rho_1^s \quad ,$$

where m_2^s is the mass of solute in the adsorbed phase in μg, m_1^s is the total mass of solvent in the adsorbed phase in grams, and ρ_1^s is the density of the adsorbed solvent at the mean temperature. Then we obtain

$$\ln c_2^s = \ln m_2^s - \ln m_1^s + \ln \rho_1^s \quad ,$$

and $$d(\ln c_2^s) = d(\ln m_2^s) - d(\ln m_1^s) \quad .$$

Thus, $$\left(\frac{\partial \ln f_2^s}{\partial c_2^s}\right)_{T,P,\sigma} dc_2^s = d(\ln m_2^s) - d(\ln m_1^s) = \frac{dm_2^s}{m_2^s} - \frac{dm_1^s}{m_1^s} \quad . \tag{8}$$

At this point we may equate equations (3) and (4) because of the equilibrium condition. Then we substitute equations (5), (6), (7), and (8) into the resulting equation. We will consider that the adsorption process occurs at constant pressure, and, in addition, we will maintain the condition that $d\sigma = 0$. Therefore, we have

$$\left(\frac{\bar{H}_2^* - \bar{H}_2}{RT^2}\right)dT + \frac{dm_2}{m_2} - \frac{dm_1}{m_1} = \left(\frac{\bar{H}_2^* - \bar{H}_2^s}{RT^2}\right)dT + \frac{dm_2^s}{m_2^s} - \frac{dm_1^s}{m_1^s} \quad . \tag{9}$$

Rearranging we obtain

$$\left(\frac{\bar{H}_2^s - \bar{H}_2}{RT^2}\right)dT = \left(\frac{dm_2^s}{m_2^s} - \frac{dm_2}{m_2}\right) - \left(\frac{dm_1^s}{m_1^s} - \frac{dm_1}{m_1}\right) \quad . \tag{10}$$

We define $\Delta\bar{H}_\sigma = \bar{H}_2^s - \bar{H}_2$, because $\Delta\bar{H}_\sigma$ is the quantity representing the differential heat of adsorption when σ is held constant. Recognizing that $dm_2^s = - dm_2$, and that $dm_1^s = - dm_1$, we see that

$$\frac{\Delta\bar{H}_\sigma}{RT^2}\, dT = - dm_2\left(\frac{m_2 + m_2^s}{m_2^s \; m_2}\right) + dm_1\left(\frac{m_1 + m_1^s}{m_1^s \; m_1}\right)$$

Now, $m_2 + m_2^{s} = m_2^{\circ}$, and $m_1 + m_1^{s} = m_1^{\circ}$, where m_2° and m_1° represent the total mass in μg and in grams in the system of the solute and solvent, respectively. Thus,

$$\frac{\Delta\bar{H}_{\sigma}}{RT^2}\, dT = -\, dm_2 \left[\frac{m_2^{\circ}}{(m_2^{\circ} - m_2)m_2} \right] + dm_1 \left[\frac{m_1^{\circ}}{(m_1^{\circ} - m_1)m_1} \right] .$$

Upon integration between the limits of T_1 and T_2, we obtain

$$\frac{\Delta\bar{H}_{\sigma}(T_2 - T_1)}{RT_2T_1} = \ln \left(\frac{m_2^{\circ} - m_2}{m_2} \right) \Bigg|_{m_2 \text{ at } T_1}^{m_2 \text{ at } T_2} - \ln \left(\frac{m_1^{\circ} - m_1}{m_1} \right) \Bigg|_{m_1 \text{ at } T_1}^{m_1 \text{ at } T_2} .$$

And since $m_1^{\circ} - m_1 = m_1^{s}$, and $m_2^{\circ} - m_2 = m_2^{s}$, the result is

$$\frac{\Delta\bar{H}_{\sigma}(T_2 - T_1)}{RT_2T_1} = \ln \left[\frac{(m_2^{s}/m_2)_{T_2}}{(m_2^{s}/m_2)_{T_1}} \right] - \ln \left[\frac{(m_1^{s}/m_1)_{T_2}}{(m_1^{s}/m_1)_{T_1}} \right] .$$

Considering that we are dealing with dilute solutions we may assume for levels of adsorption considerably less than a full monolayer coverage by the solute, that

$$\frac{(m_1^{s}/m_1)_{T_2}}{(m_1^{s}/m_1)_{T_1}} \approx 1 .$$

Thus, the final result for dilute solutions is

$$\Delta\bar{H}_{\sigma} = \frac{RT_1T_2}{T_2 - T_1} \ln \left[\frac{(m_2^{s}/m_2)_{T_2}}{(m_2^{s}/m_2)_{T_1}} \right] . \qquad (11)$$

To use equation (11) several values of σ must be calculated from the Gibbs equation (for dilute solutions) for each isotherm. This form of the Gibbs equation is given by equation (17). Then, by plotting these values of σ versus corresponding values for m_2^s/m_2, one can obtain values for m_2^s/m_2 at two temperatures at constant spreading pressure. With these pairs of values for m_2^s/m_2 one can easily solve for $\Delta\bar{H}_\sigma$. From the derivation of equation (11) it is seen that $\Delta\bar{H}_\sigma$ is equal to the difference between the partial molar enthalpy of the solute in the adsorbed phase and that of the solute in the bulk phase at equilibrium. The partial molar entropy change at equilibrium ($\Delta\bar{S}_\sigma$) may be easily determined once $\Delta\bar{H}_\sigma$ is known from the relation $\Delta\bar{H}_\sigma = T\Delta\bar{S}_\sigma$, because $\Delta\bar{G} = 0$ at any point on the isotherm.

It is interesting to note from the preceding development that if Γ (here, c_2^s) had been held constant, but σ permitted to vary (as is done in obtaining isosteric heats), one would not obtain a definition of Q from which the enthalpy and entropy changes could be readily calculated using ordinary experimental data. This is because the expression given by equation (9) would then include the term $(\partial \ln f_2^s/\partial\sigma)_{T,P,c_2^s}\, d\sigma$, while the term $\left[dm_2^s/m_2^s - dm_1^s/m_1^s\right]$ would be deleted.

A solubility-corrected differential heat of adsorption may also be derived for adsorption from solution. Kurlyandskaya and Martynov (5) have related the differential heat of solution (Q_s) and the differential heat of adsorption (Q_a) by defining a quantity Q', the differential heat of the hypothetical solid-adsorbent transition. Accordingly,

$$Q_a = Q' - Q_s \quad . \tag{12}$$

Q' is a heat of adsorption which, unlike Q_a, is independent of the temperature-solubility relationship.

We may identify Q_a, Q_s, and Q' with $\Delta\bar{H}_\sigma$, $\Delta\bar{H}_s$, and $\Delta\bar{H}'$, respectively. $\Delta\bar{H}_\sigma$ is the differential heat of adsorption at constant spreading pressure and was defined above as

$$\Delta\bar{H}_\sigma = \bar{H}_2{}^s - \bar{H}_2 \qquad (13)$$

where $\bar{H}_2$ and $\bar{H}_2{}^s$ are the partial molar enthalpies of the solute in the bulk phase and in the adsorbed phase, respectively. Now $\Delta\bar{H}_s$ is defined as the change in the partial molar heat content of the solute accompanying solution.

$$\Delta\bar{H}_s = \bar{H}_2 - \bar{H}_s\ , \qquad (14)$$

where $\bar{H}_s$ is the molar enthalpy of the pure undissolved solute. By adding equations (13) and (14) we obtain

$$\Delta\bar{H}' = \bar{H}_2{}^s - \bar{H}_s \qquad (15)$$

which corresponds with the definition of Q'.

It is readily apparent that by plotting isotherms at several temperatures, first as x/m versus c, and then as x/m versus c/c_o, the relative magnitude of $\Delta\bar{H}_\sigma$ and $\Delta\bar{H}'$ could be qualitatively perceived. Here c_o is the concentration of solute in the solvent saturated at the specified temperature.

$\Delta\bar{H}'$ can be calculated by means of a modification of equation (11). In place of m_2 we substitute m_2/m_o (comparable to c/c_o) where m_o is the total mass of solute which the given solution volume will hold at saturation at the given temperature. Thus, we have

$$\Delta\bar{H}' = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{\left[(m_2{}^s/m_2)m_o\right]_{T_2}}{\left[(m_2{}^s/m_2)m_o\right]_{T_1}}\ . \qquad (16)$$

From equation (16) it can be shown that

$$\Delta\bar{H}' = \frac{RT_1T_2}{T_2 - T_1} \ln\left[\frac{(m_2^{s}/m_2)_{T_2}}{(m_2^{s}/m_2)_{T_1}}\right] + \frac{RT_1T_2}{T_2 - T_1} \ln\left[\frac{(m_o)_{T_2}}{(m_o)_{T_1}}\right] .$$

The last term on the right-hand side is equal to $\Delta\bar{H}_s$ for a dissolved solute in a solution obeying Henry's law in equilibrium with undissolved solute (4). The first term on the right-hand side is just $\Delta\bar{H}_\sigma$. Thus, we see that the expression on the right-hand side of equation (16) is correct for determining $\Delta\bar{H}'$.

Results and Discussion

Values for $\Delta\bar{H}_\sigma$ and $\Delta\bar{H}'$ at four or more magnitudes of total surface free energy change ($A_T\sigma$) were calculated from equations (11) and (16), respectively. (A_T represents the total surface area of the adsorbent in the flask.) As described in connection with equation (11) it was necessary to calculate a value for the total surface energy change ($A_T\sigma$) for each experimental point by means of the Gibbs equation. Then, values of m_2^s/m_2, or $(m_2^s/m_2)m_o$, were calculated for each point. Plots of $A_T\sigma$ versus m_2^s/m_2, or $(m_2^s/m_2)m_o$, were made for each isotherm. Then for different temperatures of the same system m_2^s/m_2 values at constant values of $A_T\sigma$ were read off the graphs, and the $\Delta\bar{H}_\sigma$ values were calculated directly.

The calculation of $A_T\sigma$ values was performed in the following manner. The Gibbs adsorption equation for dilute solutions may be expressed as

$$\sigma = RT \int_0^a \Gamma_2 d\ln a \quad . \qquad (17)$$

Now, we shall assume that $m \cong a$, where m is the molality in moles solute per 1000 grams of solvent. Also, we assume that for dilute solutions

$$\Gamma_2 = n_2^{*} / A_T \ ,$$

where n_2^{*} is the total number of moles of solute transferred from the bulk solution to the adsorbed phase during adsorption, and A_T is the total surface area of the amount of adsorbent in the system. Then the total free energy change at the surface is $A_T\sigma$ and

$$A_T\sigma = RT \int_0^m n_2^{*} \, d\ln m \ . \qquad (18)$$

Now,

$$n_2^{*} = \frac{(x/m)(5) \times 10^{-6}}{M_2} \qquad (19)$$

where x/m is the number of micrograms of solute per gram of adsorbent transferred from the bulk solution to the solid surface, 5 is the number of grams of adsorbent in the system, 10^{-6} is the number of grams per microgram, and M_2 is the molecular weight of the solute. Further, for dilute solutions

$$m \cong \frac{c \times 10^{-3}}{M_2 \rho_{soln}} \ , \qquad (20)$$

where c is the equilibrium bulk concentration in mg/l, 10^{-3} is the number of gm/mg., and ρ_{soln} is the density of the solution. Then,

$$dm = \frac{dc}{\rho_{soln} M_2 \times 10^{3}} \ . \qquad (21)$$

Substituting equations (19), (20), and (21) into equation (18), we have

$$A_T\sigma = RT\int_0^c \frac{5 \times 10^{-6}(x/m)}{M_2 c}\, dc$$

$$A_T\sigma = \frac{5 \times 10^{-6}}{M_2}\, RT\int_0^c \frac{(x/m)}{c}\, dc \; .$$

Now, for the isotherms, or portions of isotherms, which yield linear log-log plots, $x/m = kc^{1/n}$. Thus,

$$A_T\sigma = \frac{5 \times 10^{-6}}{M_2}\, RT\int_0^c \frac{kc^{1/n}}{c}\, dc$$

and

$$A_T\sigma = \frac{5 \times 10^{-6}}{M_2}\, RTk\left[\frac{1}{(1/n)}\, c^{1/n}\Big|_0^c\right]$$

The result is

$$A_T\sigma = \frac{(5 \times 10^{-6})RTkn}{M_2}\, c^{1/n} \; . \qquad (22)$$

By means of equation (22) the values of $A_T\sigma$ were calculated for each isotherm. The calculation of these values is summarized in table 1.

Values of m_2^s/m_2 were calculated assuming that the volume of the adsorbed layer was negligible. Thus, $m_2^s/m_2 = \frac{5(x/m)}{25c} = \frac{kc^{1/n}}{5c}$, where 5 is the number of grams of adsorbent and 25 the number of milliliters of solution in each system.

(Insert Table 1)

From table 1 the values of $A_T\sigma$ were plotted against values of m_2^s/m_2 and $(m_2^s/m_2)m_o$.

(Insert Figures 1a, 1b, 2a, 2b.)

Examples of such plots are shown in figures 1a, 1b, 2a, and 2b. In general, the relative positions of the constant-temperature curves for a given system are reversed when $A_\gamma\sigma$ is plotted against $(m_2^s/m_2)m_o$ rather than m_2^s/m_2. For the systems demonstrating near superimposition of the isotherms in the plots of x/m vs. c/c_o, we find that the $A_\gamma\sigma$ versus $(m_2^s/m_2)m_o$ curves intersect at some point as in figure 2b. This, of course, results in a change in sign of the calculated $\Delta\bar{H}'$ values. All the curves exhibit a similar shape. The shape of the curves shows that as the surface coverage, or $A_\gamma\sigma$ value, becomes small, the ratio m_2^s/m_2 tends to increase more and more. At higher surface coverages, m_2^s/m_2 values change only slightly with changes in $A_\gamma\sigma$.

(Insert Figures 3 and 4)

In figures 3 and 4 the variation of $\Delta\bar{H}_\sigma$ as a function of surface coverage $(A_\gamma\sigma)$ is shown graphically for each system. Figure 5 shows the variation of $\Delta\bar{H}'$ with $A_\gamma\sigma$. It is noteworthy that $\Delta\bar{H}_\sigma$ in figure 4 (the γ-BHC-Staton

(Insert Figure 5)

peaty muck-hexane system) declines rapidly with an increase in surface free energy, while the curve for the γ-BHC-Staton peaty muck-water system (figure 3) descends very gradually. The cause of this difference is in the nature of the sites on which γ-BHC is adsorbed on this adsorbent from the two solvents. γ-BHC molecules in an aqueous medium would tend to adsorb on sites in the organic fraction while in a hexane medium they would tend to adsorb on the inorganic fraction.

On the basis of this hypothesis, it appears from the graphs of the two systems (hexane and water) that in the low range of surface coverage studied, site energies very significantly in the inorganic fraction, but only slightly in the organic fraction of Staten peaty muck. This conclusion appears to be confirmed further by the definite decline in the curves for silica gel and bentonite in figure 3. These adsorbents, representing two types of soil inorganic fractions, apparently have a greater range of site energies for γ-BHC adsorbed from water, than do Staten peaty muck and Venado clay. In the latter adsorbents organic matter obviously is important for providing adsorption sites for γ-BHC in water.

Figure 5 shows that the curves for aqueous β-BHC are somewhat higher than those for aqueous γ-BHC in the case of silica gel and Ca-Bentonite, while the curves for aqueous β-BHC on Venado clay and Staten peaty muck are in a definitely lower $\bar{H}'$ range than those for aqueous γ-BHC. An explanation may be had by assuming initially that there is a higher molar enthalpy for β-BHC in the pure solid state than for solid γ-BHC. The energy of γ-BHC in the solid state is considered to be lower than β-BHC because of the higher intermolecular attraction between the molecules of the former. If this assumption is made, then one is led to conclude from the curves in figure 5 that the energy of β-BHC adsorbed on silica gel or bentonite is a great deal more than for γ-BHC on the same adsorbents. It is possible, further, that since the non-polar portions of the organic fractions may provide sites for both aqueous β-BHC and γ-BHC on Venado clay and Staten peaty muck, the energy of the β-BHC isomer adsorbed on these adsorbents may be roughly the same as that of the γ-BHC isomer. These tentative conclusions can perhaps be best elucidates through the use of the hypothetical bar graphs in figure 6. These represent plausible interpretations of the curves in figure 5.

(Insert Figure 6)

The magnitude of $\bar{H}_s$ for γ-BHC and for δ-BHC is shown to be constant for all three adsorbent systems.

At the constant coverage to which figure 6 applies there is an extremely high affinity of the surface of silica gel for γ-BHC molecules. But at higher surface coverages figure 5 shows that the average affinity is reduced. And at $A_{\Gamma}\sigma = 12 \times 10^{-5}$ calories, the partial molar enthalpy of adsorbed γ-BHC molecules is 500 calories greater than the molar enthalpy of pure solid γ-BHC. A similar phenomenon occurs in the case of δ-BHC adsorption from water on silica gel and Staten peaty muck.

(Insert Tables 2 and 3)

The calculated values of $\Delta\bar{H}_{\sigma}$ and $\Delta\bar{H}'$ are presented in tables 2 and 3, together with values for $\Delta\bar{S}_{\sigma}$ and $\Delta\bar{S}'$, respectively. These changes in partial molar entropy were determined from the relations $\Delta\bar{H}_{\sigma} = T\Delta\bar{S}_{\sigma}$, and $\Delta\bar{H}' = T\Delta\bar{S}'$, which hold for any point on an isotherm. Isosteric heats (Q_{Γ}) were also determined. These were calculated by obtaining values for equilibrium concentration at two temperatures at a constant x/m values and then applying equation (1). These are reported in table 4. Comparison of tables 2 and 4 show that

(Insert Table 4)

for each system the Q_Γ values are of the same order of magnitude as the $\Delta\bar{H}_\sigma$ values. But a fact that might offer discouragement to the use of isosteric heats for approximating the $\Delta\bar{H}$ of adsorption is that in five cases the trend of the Q_Γ values with increasing surface coverage is different from the trend of the $\Delta\bar{H}_\sigma$ values. Thus, although the order of magnitude of $\Delta\bar{H}_\sigma$ at a given surface coverage can be reasonably estimated for these systems by the isosteric heat, the direction of change of $\Delta\bar{H}_\sigma$ with surface coverage cannot be estimated with assurance by means of Q_Γ values.

A consideration of the $\Delta\bar{S}'$ values in table 3 reveal that, with the exception of the γ-BHC-Venado clay-water system, the values of $\Delta\bar{S}'$ increase steadily with increasing surface coverage. This is fully understandable when one recognizes that $\Delta\bar{S}' = \bar{S}_2^s - \bar{S}_s$, where $\bar{S}_2^s$ is the partial molar entropy of the solute in the adsorbed phase and $\bar{S}_s$ is the molar entropy of the solute in the pure, undissolved solid state. Entropy would ordinarily increase in the transfer on dn moles of solute from the pure solid state to the adsorbed state. Even with the almost inevitable lack of translational freedom and the existence of some polar orientation of the solute molecules adsorbed on the adsorbent, the number of rotational and vibrational degrees of freedom in the adsorbed state undoubtedly exceeds that available to the solute in the solid state. It can also be recognized that the number of degrees of freedom of the adsorbed molecules on the average would tend to increase as surface coverage increases. Assuming a range of site energies for the adsorbent, with increased coverage the adsorbed molecules would tend to approach the number of degrees of freedom possessed by the solute molecules in the bulk solution. Ordinarily one would expect at equilibrium that there would exist the greatest freedom for the solute molecules in the bulk solution rather than in the adsorbed state. Reference to table 2 shows indeed that, with the exception of the β-BHC-bentonite-water system, all the $\Delta\bar{S}_\sigma$ values $(\bar{S}_2^s - \bar{S}_2)$ are negative. β-BHC molecules apparently possess a much greater number of degrees of freedom and/or a greater magnitude of configurational entropy when adsorbed on Ca-bentonite compared to the other adsorbents. High values for $\bar{S}_2^s$ may also be deduced from the high values of $\Delta\bar{S}'$ for γ-BHC adsorption from water on Ca-Venado clay and Ca-bentonite seen in table 3.

Low $\Delta\bar{S}'$ values for both γ- and β-BHC in the aqueous silica gel systems are seen in table 3. It would appear that the two BHC isomers adsorbed on silica gel most nearly approach the degree of order (lack of probable degrees of freedom) of the pure solid state. This could indicate a considerable degree of orientation of the adsorbed molecules on the silica surface, or some other type of immobilization of the molecules such as to reduce their freedom. The γ-BHC molecules adsorbed from water on Venado clay, Staten peaty muck, and bentonite, by contrast, appear to have considerable freedom, including the possibility of some two-dimensional translational freedom.

Summary

Isosteric heats (Q_Γ) and heats obtained for a constant change of interfacial tension were calculated for the adsorption of γ and β-BHC on inorganic and organic surfaces. Unlike the isosteric heats, the latter heats, designated as $\Delta\bar{H}_\sigma$ were shown to represent the true difference at equilibrium between the partial molar enthalpy of the adsorbed solute and that of the solute in solution. Values of $\Delta\bar{H}_\sigma$ were calculated from the equation

$$\Delta\bar{H}_\sigma = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{(m_2^s/m_2)_{T_2}}{(m_2^s/m_2)_{T_1}} \quad ,$$

where m_2 and m_2^s refer to the total mass of solute in solution and in the adsorbed phase at equilibrium, respectively. This equation was derived for dilute solutions assuming Henry's law holds for the solute both in solution and in the adsorbed phase. Calculated Q_Γ values were observed to be of the same order of magnitude for each isotherm as the $\Delta\bar{H}_\sigma$ values, but the trend of Q_Γ with changing surface coverage was observed to differ in some cases from that of the $\Delta\bar{H}_\sigma$ values.

The decrease of $\Delta\bar{H}_\sigma$ with surface coverage was shown in γ-BHC systems to be clear and definite in the case of adsorption on bentonite and silica gel from water, and on Staten peaty muck from hexane. But a very gradual $\Delta\bar{H}_\sigma$ decrease was observed for γ-BHC adsorption in the Staten peaty muck-water and Venado clay-water systems. This led to the conclusion that in the surface coverage range studied there is a definite range site energies on inorganic surfaces, but a relatively small range of site energies on the organic fractions of the adsorbents. Values for $\Delta\bar{S}_\sigma$ were calculated from the fact that $\Delta\bar{H}_\sigma = T\Delta\bar{S}_\sigma$ at any point on the isotherm.

Values for $\Delta\bar{H}'$ were calculated from the above equation for $\Delta\bar{H}_\sigma$ with the exception that reduced mass in solution, m_2/m_o, was substituted for m_2, where m_o is the total mass of solute which the given solution volume will hold at saturation at the given temperature. $\Delta\bar{H}'$ is defined as

$\Delta\bar{H}' = \bar{H}_2^s - \bar{H}_s$, where $\bar{H}_2^s$ is the partial molar heat content of the solute adsorbed on the adsorbent at equilibrium and $\bar{H}_s$ is the molar enthalpy of the solid solute. Assuming that a higher molar enthalpy holds for solid β-BHC than for solid γ-BHC, a graphical representation was presented to explain differences in $\Delta\bar{H}'$ values between aqueous β-BHC and aqueous γ-BHC systems. Values of $\Delta\bar{S}'$ were observed to increase uniformly with increasing surface coverage. Assuming a range of energy sites, it is to be expected that as coverage increases the average number of degrees of freedom of the adsorbed molecules will increase. In contrast, the $\Delta\bar{S}_\sigma$ values were negative, with the exception of the α-BHC-bentonite-water system. More freedom for the solute molecules would be expected in solution than in the adsorbed state. It is likely that the configurational entropy of α-BHC adsorbed from water on bentonite is quite high. The lowest $\Delta\bar{S}'$ values were obtained for γ-BHC and β-BHC adsorption from water on silica gel.

Acknowledgement

The authors gratefully acknowledge support of the Federal Water Pollution Control Administration through Training Grant 5T1-WP-07 and Research Grant WP-0008.

References

1. Mills, A. C., Dissertation, University of California, 1967.

2. Thomas, T. L., Thermodynamics of Adsorption from Solution. Ph.D. Thesis, University of Michigan, 1949.

3. Hill, T. L., Statistical mechanics of adsorption. V. Thermodynamics and heat of adsorption. Journal of Chemical Physics 17(6), 520-535 (1949).

4. Klotz, I. M., Chemical Thermodynamics, W. A. Benjamin, Inc., New York, 1964.

5. Kurlyandskaya, I. I., and Yu. M. Martynov, Adsorption of sparingly soluble substances. Russian Journal of Physical Chemistry 38(4), 571-573 (1964).

Table 1

Calculation of Values of $+A_T\sigma$ and Associated Values of m_2^s/m_2 and $(m_2^s/m_2)m_o$

$$\left(Z = \left[\frac{5 \times 10^{-6}}{M_2}\right] RT\right)$$

Ca-Staten peaty muck

Isomer and Solvent	T (°C)	$Z \times 10^6$	Freundlich k	n	$c^{1/n}$	$+A_T\sigma \times 10^5$	m_2^s/m_2	$\frac{m_2^s}{m_2/m_o}$
γ-BHC in water	10	9.673	377	1.046	.000745	.284	105.2	
					.006148	2.34	95.26	
					.01291	4.92	92.09	
					.02669	10.18	89.01	
					.06539	24.94	85.45	
	20	10.0149	331	1.0322	.000832	.285	83.20	17,722
					.007375	2.52	77.53	16,514
					.01443	4.94	75.87	16,160
					.02920	9.99	74.12	15,787
					.07506	25.68	71.95	15,326
	30	10.3565	269	1.0198	.001024	.291	61.61	20,239
					.008790	2.50	59.08	19,409
					.01809	5.14	58.21	19,121
					.03616	10.27	57.45	18,874
					.09130	25.94	56.41	18,530
	40	10.6982	197	1.0174	.001367	.293	44.22	
					.01265	2.71	42.50	
					.02384	5.11	42.05	
					.04700	10.08	41.56	
					.1255	26.91	40.84	
β-BHC in water	20	10.0149	456	1.0531	.000801	.386	133.2	8,993
					.002147	1.03	126.3	8,527
					.003868	1.86	122.5	8,268
					.004629	2.23	121.3	8,188
	30	10.3565	437	1.0104	.0008524	.390	94.02	8,485
					.002090	.956	93.19	8,411
					.004014	1.84	92.56	8,354
					.004967	2.27	92.37	8,336
γ-BHC in hexane	10	9.6733	.974	1.1285	.10814	.115	.259	63,274
					.45774	.487	.215	52,560
					.86338	.918	.199	48,440
					2.3413	2.49	.174	42,560
					6.8850	7.32	.152	37,100
	20	10.0149	.823	1.0696	.09855	.087	.193	67,560
					.45477	.401	.174	60,750
					.87034	.767	.166	58,060
					2.4315	2.14	.155	54,010
					7.6486	6.74	.143	49,920

Table 1 (cont.)

Ca-Venado clay

Isomer and solvent	T (°C)	Σ x 10^6	Freundlich k	n	$c^{1/n}$	$+\Delta_{\gamma}\sigma$ x 10^5	m_2^s/m_2	$\frac{m_2^s}{m_2/m_o}$
γ-BHC in water	10	9.6733	53.8	1.1550	.005118 .04143 .08475 .1710 .4431	.308 2.49 5.09 10.28 26.63	24.36 17.63 15.77 14.16 12.21	
	20	10.0149	45.7	1.1888	.005969 .04901 .1005 .1955 .5128	.325 2.66 5.47 10.64 27.90	24.03 16.16 14.11 12.44 10.37	5,122 3,442 3,006 2,650 2,210
	30	10.3565	41.3	1.1832	.006496 .05408 .11025 .21703 .55041	.329 2.74 5.58 10.98 27.86	20.77 14.10 12.38 10.93 9.21	6,824 4,630 4,066 3,592 3,027
	40	10.6982	36.1	1.1813	.007345 .06135 .12448 .23798 .62540	.335 2.80 5.68 10.86 28.53	17.62 11.97 10.54 9.37 7.86	
β-BHC in water	20	10.0149	62.8	1.1618	.005800 .014349 .027066 .033168	.424 1.05 1.98 2.42	28.91 24.96 22.53 21.80	1,951 1,685 1,521 1,472
	30	10.3565	60.2	1.1322	.006104 .014061 .028779 .034357	.431 .992 2.03 2.42	23.63 21.16 19.25 18.80	2,133 1,910 1,737 1,697

Ca-bentonite

Isomer and solvent	T (°C)	Σ x 10^6	Freundlich k	n	$c^{1/n}$	$+\Delta_{\gamma}\sigma$ x 10^5	m_2^s/m_2	$\frac{m_2^s}{m_2/m_o}$
γ-BHC in water	20	10.0149	2.92	1.1280	.044463 .33642 .65046 1.2117 2.8881	.147 1.11 2.14 4.00 9.53	.870 .671 .617 .570 .510	185.2 143.0 131.6 121.4 108.6
	30	10.3565	2.71	1.0978	.043544 .34168 .65463 1.2425 3.0247	.134 1.05 2.02 3.83 9.32	.736 .602 .565 .531 .486	241.9 197.8 185.6 174.3 159.8
β-BHC in water	19.8	10.0081	3.96	1.1583	.05233 .12566 .22725 .26689	.240 .577 1.04 1.225	1.263 1.100 1.002 .976	85.28 74.24 67.61 65.90
	30	10.3565	4.46	1.1299	.04754 .11532 .21165 .24491	.248 .602 1.10 1.28	1.325 1.181 1.091 1.071	119.6 106.6 98.5 96.6

Table 1 (cont.)

Silica gel

Isomer and solvent	T (°C)	$Z \times 10^6$	Freundlich k	n	$c^{1/n}$	$+\Delta_T\sigma \times 10^5$	m_2^s/m_2	$\frac{m_2^s}{m_2/m_o}$
γ-BHC in water	20	10.0149	6.88	1.0655	.025966	.191	1.748	372.3
					.21334	1.57	1.523	324.3
					.42414	3.11	1.455	310.0
					.82950	6.090	1.393	296.7
					2.0755	15.24	1.312	279.4
	30	10.3565	4.62	1.0447	.031281	.156	1.078	354.2
					.26398	1.32	0.981	322.2
					.51169	2.558	0.952	312.8
					1.0214	5.11	0.923	303.2
					2.5437	12.72	0.886	291.1
β-BHC in water	19.8	10.0081	2.13	1.0294	.054893	.120	0.464	31.31
					.13997	.307	0.451	30.46
					.26143	.574	0.443	29.91
					.30356	.666	0.441	29.78
	30	10.3565	1.64	1.0152	.057751	.100	0.342	30.91
					.14622	.252	0.338	30.48
					.27538	.475	0.334	30.19
					.32452	.560	0.334	30.12

Table 2

Constant Surface Tension Heats and Entropy Changes in Adsorption ($\Delta\bar{H}_\sigma$ and $\Delta\bar{S}_\sigma$)

(in calories/mole and calories/deg-mole)

System	Chosen $A_\Gamma\sigma$ x 10^5	15°C		25°C		35°C	
		$\Delta\bar{H}_\sigma$	$\Delta\bar{S}_\sigma$	$\Delta\bar{H}_\sigma$	$\Delta\bar{S}_\sigma$	$\Delta\bar{H}_\sigma$	$\Delta\bar{S}_\sigma$
γ-BHC-Ca-Staten peaty muck-water	0.6	-3,510	-12.2	-5,210	-17.5	-6,250	-20.3
	3	-3,320	-11.5	-4,810	-16.1	-6,170	-20.0
	10	-3,040	-10.5	-4,510	-15.1	-6,120	-19.8
	25	-2,810	- 9.76	-4,300	-14.4	-6,160	-20.0
γ-BHC-Ca-Venado clay-water	0.6	- 440	- 1.52	-2,220	- 7.43	-3,170	-10.3
	3	-1,690	- 5.87	-2,390	- 8.02	-2,950	- 9.56
	10	-1,980	- 6.84	-2,240	- 7.50	-2,830	- 9.19
	25	-2,280	- 7.90	-2,140	- 7.19	-3,080	- 9.98
γ-BHC-Ca-bentonite-water	0.3			-2,760	- 9.25		
	2			-1,700	- 5.70		
	5			-1,260	- 4.23		
	9			- 845	- 2.83		
γ-BHC-Silica gel-water	0.3			-8,430	-28.3		
	2			-7,810	-26.2		
	6			-7,410	-24.8		
	12			-7,140	-23.9		
γ-BHC-Ca-Staten peaty muck-hexane	0.3	-4,240	-14.7				
	0.6	-3,450	-12.0				
	1.5	-2,640	- 9.18				
	3.0	-2,030	- 7.04				
	6.0	-1,300	- 4.52				
β-BHC-Ca-Staten peaty muck-water	0.6			-5,840	-19.6		
	1.0			-5,390	-18.1		
	1.6			-5,080	-17.0		
	2.2			-4,810	-16.1		
β-BHC-Ca-Venado clay-water	0.6			-3,380	-11.3		
	1.0			-3,060	-10.2		
	1.6			-2,860	- 9.60		
	2.2			-2,650	- 8.90		
β-BHC-Ca-bentonite-water	0.3			1,000	3.37		
	0.5			1,260	4.22		
	0.8			1,390	5.33		
	1.2			1,680	5.65		
β-BHC-Silica gel-water	0.15			-5,220	-17.5		
	0.30			-5,050	-17.0		
	0.40			-5,080	-17.0		
	0.55			-4,900	-16.4		

Table 3

'Corrected' Constant Surface Tension Heats of Adsorption

($\Delta\bar{H}'$) and entropy changes ($\Delta\bar{S}'$)

(in calories/mole and calories/deg-mole)

System	Chosen $A_\Gamma\sigma$ $\times 10^5$	$\Delta\bar{H}'$ (25°C)	$\Delta\bar{S}'$ (25°C)
γ-BHC-Ca-Staten peaty muck-water	0.6	2,640	8.84
	3	2,860	9.60
	10	3,180	10.6
	25	3,350	11.2
γ-BHC-Ca-Venado clay-water	0.6	5,600	18.8
	3	5,340	17.9
	10	5,510	18.5
	25	5,580	18.7
γ-BHC-Ca-bentonite-water	0.3	4,320	14.5
	2	5,930	19.9
	5	6,390	21.4
	9	6,780	22.7
γ-BHC-Silica gel-water	0.3	- 945	- 3.17
	2	- 174	- 0.58
	6	211	0.71
	12	522	1.75
γ-BHC-Ca-Staten peaty muck-hexane	0.3	1,690	5.85
	0.6	2,310	8.03
	1.5	3,430	11.9
	3.0	3,960	13.7
	6.0	4,590	15.9
β-BHC-Ca-Staten peaty muck-water	0.6	- 688	- 2.31
	1.0	- 283	- 0.95
	1.6	65.1	0.22
	2.2	315	1.06
β-BHC-Ca-Venado clay-water	0.6	1,730	5.81
	1.0	2,030	6.82
	1.6	2,280	7.66
	2.2	2,450	8.23
β-BHC-Ca-bentonite-water	0.3	5,870	19.7
	0.5	6,260	21.0
	0.8	6,320	21.9
	1.2	6,710	22.5
α-BHC-Silica gel-water	0.15	- 225	- 0.75
	0.30	- 57.4	- 0.19
	0.40	0.00	0.00
	0.55	104	0.35

Table 4

Isosteric Heats of Adsorption (Q_Γ)

(in calories/mole)

System	Chosen x/m (μg/gm)	Q_Γ(15°)	Q_Γ(25°)	Q_Γ(35°)
γ-BHC-Ca-Staten peaty muck-water	5	-2,760	-4,740	-5,290
	10	-3,030	-4,720	-5,360
	15	-3,090	-4,700	-5,680
	20	-3,140	-4,440	-6,010
γ-BHC-Ca-Venado clay-water	5	-1,500	-2,600	-2,460
	10	-1,810	-2,870	-2,280
	15	-2,150	-2,770	-2,500
	20	-2,530	-2,230	-3,110
γ-BHC-Ca-bentonite-water	1		-1,980	
	3		-1,620	
	5		-1,510	
	7		-1,370	
γ-BHC-Silica gel-water	2		-7,960	
	4		-7,520	
	6		-7,450	
	8		-7,440	
	10		-7,320	
γ-BHC-Ca-Staten peaty muck-hexane	0.5	-3,120		
	2	-1,420		
	4	-1,470		
	6	-1,530		
β-BHC-Ca-Staten peaty muck-water	0.8		-4,330	
	1.2		-4,270	
	1.6		-4,590	
	2.0		-5,240	
β-BHC-Ca-Venado clay-water	0.6		-3,920	
	1.0		-3,750	
	1.2		-3,640	
	1.6		-3,410	
	1.8		-3,210	
β-BHC-Silica gel-water	0.2		-4,590	
	0.3		-4,290	
	0.4		-4,380	
	0.5		-4,770	

Figure Titles

Figure 1A. Variation of the total surface free energy ($-A_T\sigma$) with surface coverage (m_s/m) for γ-BHC adsorption from water on Ca-Staten peaty muck and Venado clay at four temperatures.

Figure 1B. Variation of $-A_T\sigma$ with surface coverage corrected for the solubility temperature interaction $[(m_s/m)m_o]$ for γ-BHC adsorption from water on Ca-Staten peaty muck and Ca-Venado clay at two temperatures.

Figure 2A. Variation of the total surface free energy with surface coverage for γ-BHC adsorption from water on Ca-bentonite and silica gel at 20°C and 30°C.

Figure 2B. Variation of $-A_T\sigma$ with $(m^s/2)m_o$ for γ-BHC adsorption from water on Ca-bentonite and silica gel.

Figure 3. Decrease in the differential enthalpy of adsorption with changes in surface free energy during adsorption of γ-BHC and β-BHC on four adsorbents.

Figure 4. Variations of the differential heat of adsorption ($\Delta\bar{\bar{H}}_\sigma$) at constant spreading pressure and the corrected differential heat of adsorption $\Delta\bar{\bar{H}}'$ with surface coverage for γ-BHC adsorption on Staten peaty muck from hexane at 15°C.

Figure 5. Variations of $\Delta\bar{\bar{H}}'$ with increasing total surface free energy for γ-BHC and β-BHC adsorption on four adsorbates.

Figure 6. Schematic representation of a possible relation between $\bar{\bar{H}}_s$, the partial molar enthalpy of pure undissolved solute and $\bar{\bar{H}}_2^s$ the partial molar enthalpy of the solute in the adsorbed phase for aqueous β-BHC and γ-BHC for three adsorbents. ($A_T\sigma = 1 \times 10^{-5}$ cal).

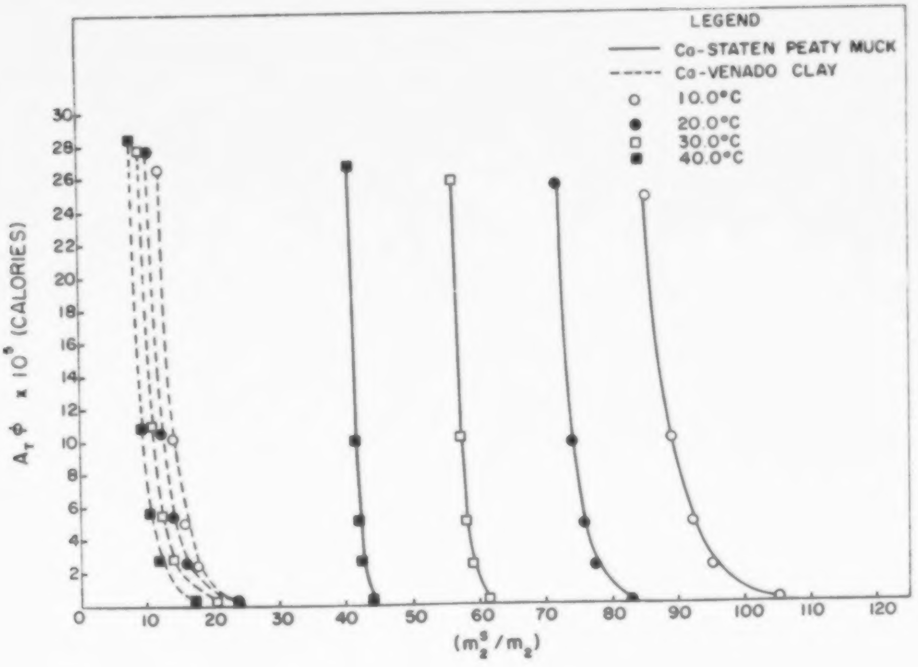


Figure 1A. Variation of the total surface free energy ($-A_T\sigma$) with surface coverage (m_s/m) for γ-BHC adsorption from water on Ca-Staten peaty muck and Venado clay at four temperatures.

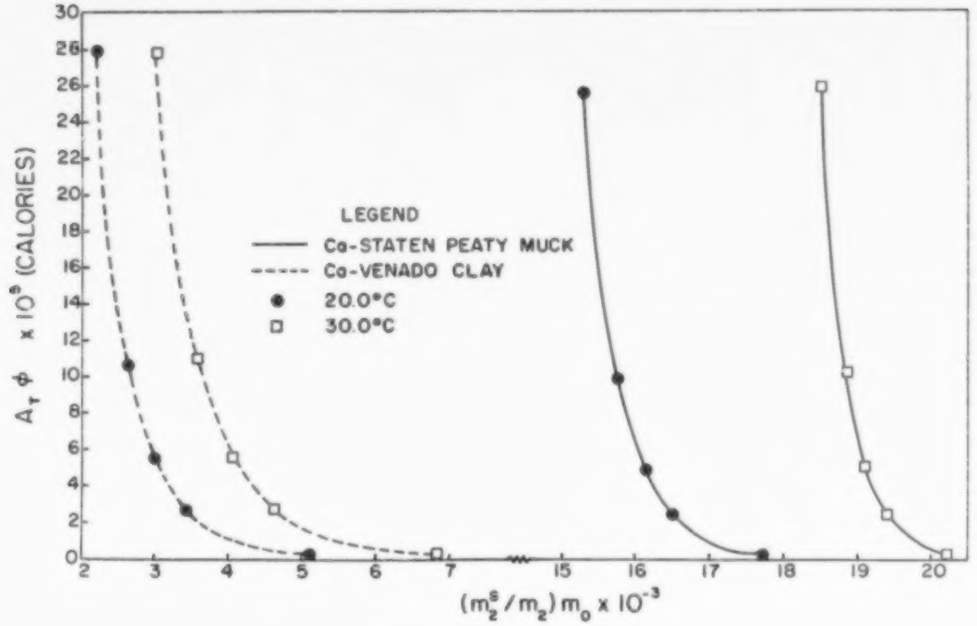


Figure 13. Variation of $-A_T\sigma$ with surface coverage corrected for the solubility temperature interaction $[(m_s/m)m_o]$ for γ-BHC adsorption from water on Ca-Staten peaty muck and Ca-Venado clay at two temperatures.

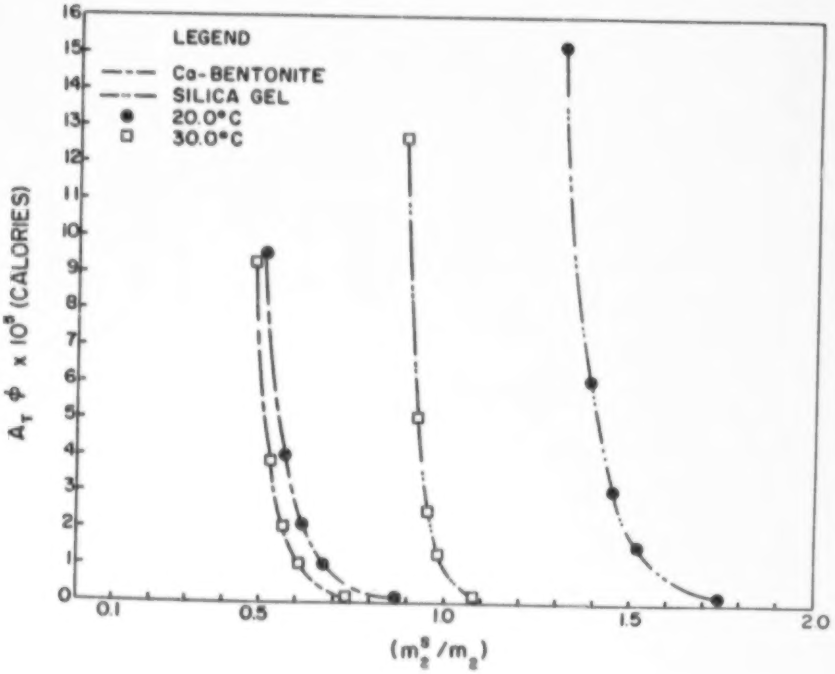


Figure 2A. Variation of the total surface free energy with surface coverage for γ-BHC adsorption from water on Ca-bentonite and silica gel at 20°C and 30°C.

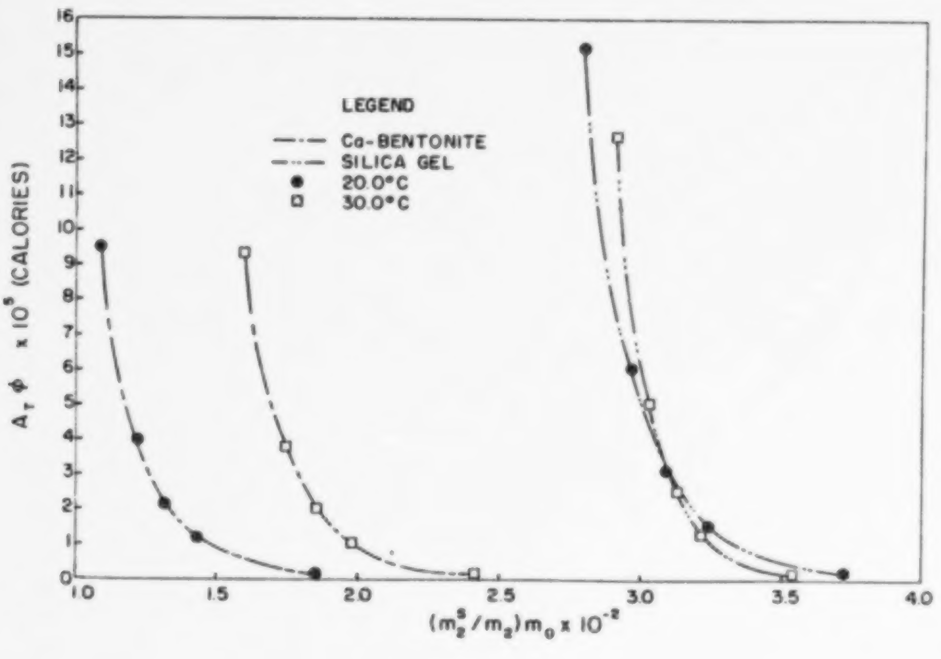


Figure 23. Variation of $-A_T\sigma$ with $(m^s/2)m_s$ for γ-BHC adsorption from water on Ca-bentonite and silica gel.

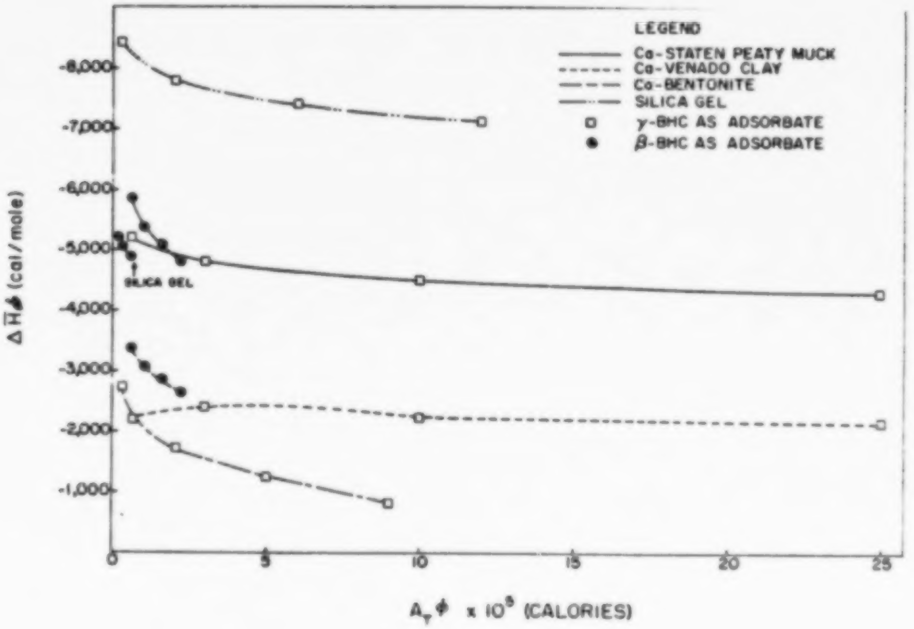


Figure 3. Decrease in the differential enthalpy of adsorption with changes in surface free energy during adsorption of γ-BHC and β-BHC on four adsorbents.

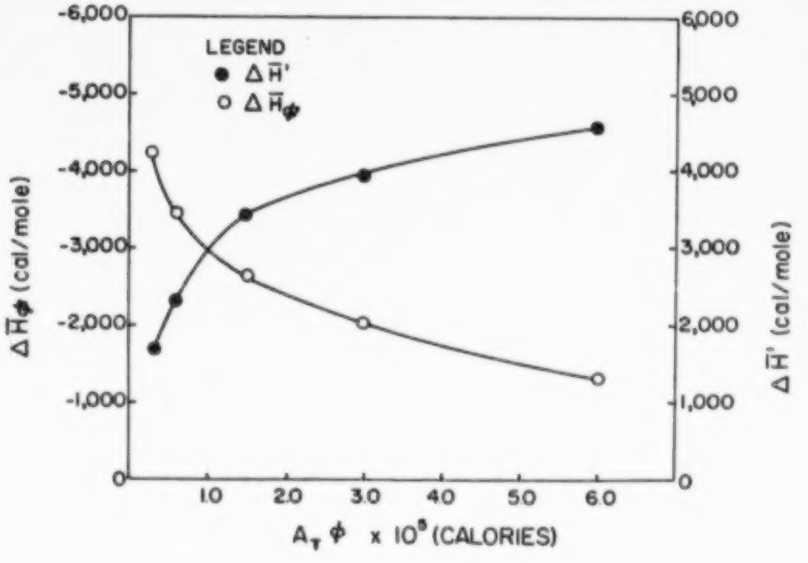


Figure 4. Variations of the differential heat of adsorption ($\Delta\bar{\bar{H}}_{\sigma}$) at constant spreading pressure and the corrected differential heat of adsorption $\Delta\bar{\bar{H}}'$ with surface coverage for γ-BHC adsorption on Staten peaty muck from hexane at 15°C.

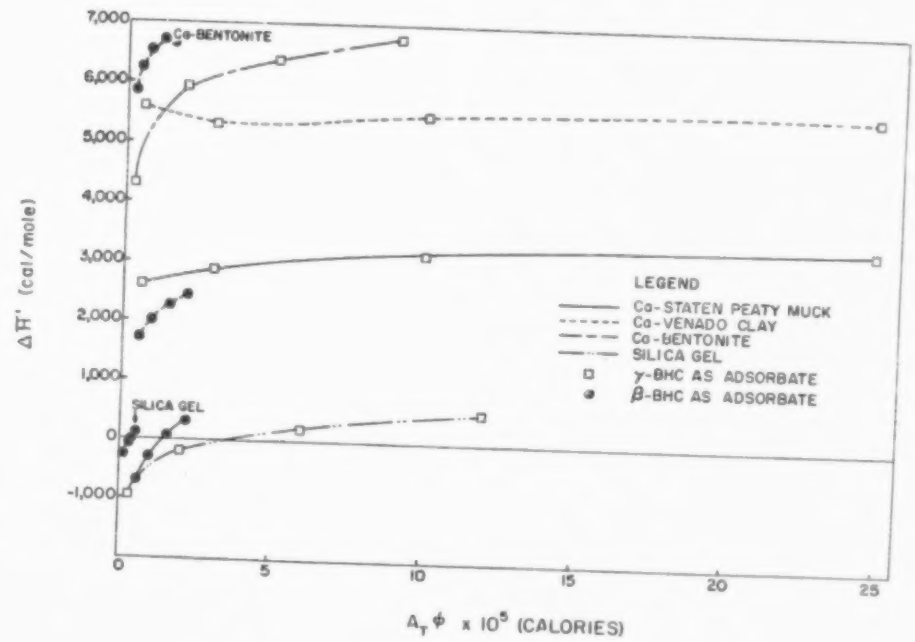


Figure 5. Variations of $\Delta\bar{H}'$ with increasing total surface free energy for γ-BHC and β-BHC adsorption on four adsorbates.

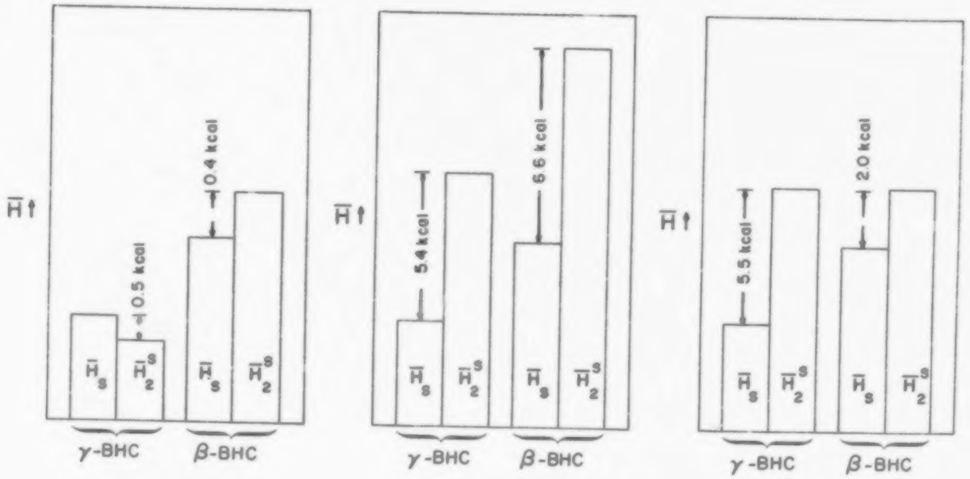

$\bar{H}\uparrow$
0.5 kcal
0.4 kcal
$\bar{H}_s$
$\bar{H}_2^s$
γ-BHC
β-BHC
$\bar{H}\uparrow$
5.4 kcal
6.6 kcal
$\bar{H}_s$
$\bar{H}_2^s$
γ-BHC
β-BHC
$\bar{H}\uparrow$
5.5 kcal
2.0 kcal
$\bar{H}_s$
$\bar{H}_2^s$
γ-BHC
β-BHC

Figure 6. Schematic representation of a possible relation between $\bar{H}_s$, the partial molar enthalpy of pure undissolved solute and $\bar{H}_2^s$ the partial molar enthalpy of the solute in the adsorbed phase for aqueous β-BHC and γ-BHC for three adsorbents. ($A_T\sigma$ = 1 x 10^{-5} cal)

Abstract

Freundlich adsorption isotherms were obtained when the gamma and beta isomers of 1,2,3,4,5,6-hexachlorocyclohexane were adsorbed from aqueous and hexane solvents on Ca-Staten peaty muck, Ca-bentonite, Ca-Venado clay and silica gel in the temperature range of 10° to 40°C. Normal (x/m VS C) and "corrected" (x/m VS c/C_0) isotherms revealed; in comparison, the temperature effect on solubility as being significant in the adsorption process. The 1/n constants of the Freundlich equation increased with temperature according to the theory of dilute solutions. When the solubility effect is removed, the adsorbability of the gamma isomer is greater possibly because it possesses a dipole moment while the beta isomer does not. It was found that at constant solution fugacities, the gamma isomer competes somewhat more effectively on Staten peaty muck with hexane than with water.

Synopsis

Normal and "corrected" Freundlich isotherms of the adsorption of gamma and beta isomers of BHC on four soil materials from water and hexane revealed the effect of solubility, the importance of differing molecular characteristics of the isomers, and the role of the solvent in the extent of adsorption.

Adsorption of Gamma- and Beta-BHC from solution. Adsorption isotherms and the solubility-Temperature Effect

by

A. G. Mills and J. W. Biggar[1]
Department of Water Science and Engineering
University of California, Davis, California 95616

In recent years the importance of pesticide for increasing crop production has led to great increases in both the types and amounts used. Numerous studies have been carried out and are in progress to find out the degree of persistence of applied herbicides, fungicides and insecticides on crops and soils. But the fate of many of these chemicals is not restricted to soils particularly if they are both persistent and somewhat mobile. Consequently, the search for the presence and behavior of these materials involves ~~with~~ soils, crops and water supplies (Edwards 1966; Faust and Suffet 1966).

The compound, 1, 2, 3, 4, 5, 6-hexachlorocyclohexane and its beta isomer were chosen because of widespread use, moderate persistence and mobility (Edwards 1966), its dissipation in water supplies (Faust and Suffet 1966), and the opportunity to examine certain molecular properties important to their uptake and release by adsorbents. In other words, the present study attempts to examine the extent that different electrical properties of the two isomers modifies the energy of adsorption. By conducting such studies it may be possible to better predict those properties which contribute to mobility, persistence and safe utilization of the chemical.

---

[1] Investigation supported by Training Grant 5T1-WP-07 and Research Grant WP-0008 from the Federal Water Pollution Control Administration and Regional Research W-82. The senior author address is C-52 N.D. South, 7AFPRO, Extension II, New Delhi 16, India.

There are eight isomers of the chemical, two of which are being investigated here. Grades of the gamma-isomer which have a purity of 99% or higher are known as lindane. This isomer displays far greater insecticidal properties than the other isomers. Its lethal action on many insects is typically faster than that of DDT (Shepard 1957).

The molecule 1,2,3,4,5,6-hexachlorocyclohexane is not planar since the carbon ring assumes a "puckered" chair form. In the gamma-isomer three chlorine atoms are equatorial (extending out roughly from what may be considered the plane of the ring) and three chlorine atoms are axial (projecting above or below the ring). In the beta-isomer all the chlorine atoms are equatorial. Lind, Hobbs, and Gross (1950) note that since the beta isomer is centrosymmetric, the electric moment is expected to be zero and measured it as such. On the other hand, they measured a dipole moment for gamma-BHC in benzene at 30°C of 2.84 debye units.

Although a number of field experiments have been performed using lindane, no thorough laboratory experiments have come to light that would provide the information required for predicting their behavior for a wide variety of conditions. Lichenstein (1958) placed two layers of soil containing 10 ppm lindane over untreated layers in cartons. Water treatments applied revealed that most movement occurred in Plainfield sand and least in muck. Diffusion contributed to movement in non-leached soils. Gargantini, Giavotti and DeTella (1959) applied 1% and 12% BHC to surface acid sandy loam soil in 40 cm deep lysimeters. After 6 months of gently applying 1079 mm of water, 90% of the BHC was found in the top 10 cm. and 0.6% in the bottom layer. Swanson, Thorp and Friend (1954) found in leaching studies using petroleum ether that exchange resins held no lindane, organic matter seemed to have little effect in increasing adsorption, but a close correlation existed between clay content and adsorption. Other results recently summarized (Mills, 1967) include a variety of field and laboratory experiments that probably can be reconciled with additional controlled laboratory investigations.

The choice of the adsorbents and solvents to employ for the isotherm studies was made after adsorption studies were performed on a wide range of adsorbents at one temperature series. Adsorption levels were considered to be too low from benzene and ethanol solutions to permit accurate determination of isotherms over a range of low concentrations. The four adsorbents were chosen because they represent particular types of adsorbing surfaces common in soils and because they exhibited considerable affinity for γ-BHC in hexane and aqueous solutions. These adsorbents, Ca-Staten peaty muck, Ca-Venado clay, Ca-bentonite, and silica gel, represent, respectively, a high organic soil with a mixed mineral fraction, a clay soil high in montmorillonite containing a little organic matter, a montmorillonitic clay, and a crystalline silica. In addition to being representative of particular soils or soil fractions, these adsorbents showed relatively little or no tendency to catalyze decomposition of γ-BHC in hexane or water. However, it seems clear that further study of some of the other adsorbents would be useful in the future.

Isotherms for each system were obtained at two or more temperatures in the range 10°C to 40°C. Because of the limited solubility of the two isomers in water the concentration range for these isotherms was restricted to very low concentrations. The concentration range was 0.056 to 5.0 μg/ml for the initial aqueous γ-BHC solutions, and 0.075 to 0.65 μg/ml for the initial aqueous β-BHC solutions. A considerably wider concentration range was adopted for the hexane solution isotherms--0.10 to 500.0 μg/ml. Isotherms in which hexane was the solvent were obtained for the γ-BHC-Ca-Venado clay and γ-BHC-Ca-Staten peaty muck systems.

In all the isotherm studies unequivocal decomposition occurred only in the γ-BHC-Ca-Venado clay-hexane system. The isotherms for this system are, thus, difficult to interpret, because of the existence of some breakdown products in the system.

It is commonplace to observe the displacement of isotherms downward as the temperature at which adsorption is measured is increased. Contributing to this net effect for adsorption from solutions is not only the energy contributions in the adsorption reaction itself, but also the change in solubility of the solute in the solvent due to the temperature change. The principle involved is that the fugacity of a given solute in solution at a constant concentration will assume different values depending upon the temperature. And this change in fugacity with temperature may be considered to be closely related to the change in the reduced concentration, c/c_o, with temperature, where c, the solute concentration, may be considered constant, and c_o is the solubility of the solute in the solvent at a specified temperature. Thus, the fugacity, and therefore, the chemical potential, of a solute in solution at any specified concentration depends at least in part upon the solubility of the solute in the solvent as affected by the temperature as well as by the particular solvent. Since the difference between the fugacity of the solute in the bulk solution and that on the adsorbent is considered the driving force behind the adsorptive process, it is important to take into account the influence of temperature upon solute fugacity. By plotting isotherms as x/m vs. c/c_0 the effect of the energy contributions in the adsorption process apart from solubility-temperature effects may be seen qualitatively.

Experimental Methods

Solutions were prepared with a constant concentration of radiochemical of both isomers with the remainder made up with non-radioactive isomer. Five or ten gms of over lined adsorbent were weighed into flasks which were placed in the oven for several hours prior to treatment. After cooling,25 ml of the appropriate solution were added to each flask. Duplicates were used including adsorbent blanks and standard blanks. Flasks were stoppered, enclosed in polyethylene bags and immersed in baths controlled to ± 0.05°C. Following 20 hours of shaking and 50 hours of rest, the solutions were centrifuged for 20 minutes at 10,000 rpm and constant temperature. Ten ml aliquots of aqueous solvent were removed, and extracted by adding 10 ml of nanograde hexane. Analysis of the equilibrium solution was performed both by liquid scintillation (L.S.) and gas liquid chromatography (G.C.). The equilibration centrifugation, and other experiments on method have been reported elsewhere (Mills 1967). When the L.S. and G.C. concentrations disagreed by more than 10%, the latter were used as a measure of isomer in solution. This provided a means for checking on decomposition even though the L.S. analysis was more accurate and precise.

Nature of Isotherms Obtained

The normal isotherms (x/m plotted against c) are presented in figures 1a, 2a, 3a, 4a, 5a and 6a. The corresponding isotherms in which x/m values are plotted against the reduced concentration, c/c_o (hereafter designated as the 'corrected' isotherms) are shown in figures 1b, 2b, 3b, 4b, 5b and 6b. In each case c_o represents the solubility of the isomer in the particular solvent at the given temperature, as determined by the authors.

It is apparent from figures 1 and 2 that the isotherms for γ-BHC in water on all four adsorbents are nearly linear. The normal isotherms (figures 1a and 2a) show that an increase in temperature uniformly results in a lowering of adsorption for each of the systems. Proportionally, the decrease of adsorption with increased temperature is least with silica gel and greatest for Ca-bentonite. Figures 1b and 2b, the corrected isotherms, indicate the reverse with an increase in adsorption with increase in temperature. One would, thus, expect the associated differential heats of adsorption to be positive. Only in the case of silica gel is there very little increase in adsorption with increased temperature. Figure 2b indicates that adsorption in this case may proceed with essentially no heat effect, except for that involved in the solubility relationship. It would appear, then, that in these cases it is only the solubility-temperature effect which serves to make the adsorption process exothermic, while it would otherwise tend to be endothermic. The higher relative positions of the isotherms for Ca-Staten peaty muck and Ca-Venado clay, as seen in figure 1a, underscore the importance of organic matter in the adsorption of γ-BHC from water.

The adsorption of β-BHC from aqueous solutions is seen in figure 3a to parallel closely the adsorption of aqueous γ-BHC on Staten peaty muck and Venado clay. The respective slopes of the curves in figures 1a and 3a correspond very well. If the highest concentration points are neglected these β-BHC isotherms also approach a linear form. The corrected isotherms of figure 3b show that, as for the aqueous γ-BHC systems, when the solubility-temperature effect is eliminated, adsorption is no longer exothermic. In the case of the corrected isotherms on adsorption on Staten peaty muck, unlike the aqueous γ-BHC-Staten peaty muck system showed no change with temperature.

In figure 4a the normal isotherms for Ca-bentonite show that β-BHC adsorption increased slightly with temperature. This increase broadened considerably when the solubility effect was removed, as shown in figure 4b. A further difference relative to the aqueous γ-BHC systems is in the relative positions of the Ca-bentonite and silica gel isotherms. While silica gel exhibited a greater adsorption affinity for aqueous γ-BHC than did Ca-bentonite, the reverse is true for the adsorption of β-BHC. Similar to the aqueous γ-BHC case, the corrected isotherms for β-BHC on silica gel exhibit little or no temperature effect, i.e., heat effects other than those associated with solution are almost negligible.

The isotherms of γ-BHC adsorption from hexane are shown in figures 5 and 6. The lesser degree of adsorption on Ca-Staten peaty muck compared to Ca-Venado clay is apparent throughout the concentration range. The isotherms for Ca-Staten peaty muck approach linearity particularly over the lower part of the concentration range. (See figure 6a in which only the five lowest concentration points are plotted.) It is clear from the normal isotherms in figure 5a that there is no consistent effect of temperature in the adsorption on Staten peaty muck over the whole range of concentrations studied. It is possible that at a certain surface coverage or concentration range the overall adsorption process changes from an exothermic to an endothermic one, as indicated in figure 5a. But inspection of the corrected isotherms for the entire concentration range (figure 5b) reveals that increasing temperature results uniformly in increased adsorption over the entire range. Over the lower part of the concentration range (figures 6a and 6b) both the normal and corrected isotherms reveal a uniform temperature effect and one that corresponds well with the temperature behavior of aqueous γ-BHC on the same adsorbent.

Freundlich Constants

The Freundlich equation for isotherms is frequently applicable to adsorption from solutions. It is written as

$$x/m = kc^{1/n}, \qquad (1)$$

where k and n are constants. From the form of the equation it is apparent, that, unlike the Langmuir isotherm, no limiting saturation value is obtained. The equation is essentially an empirical one, based on no theoretical model. Kipling (1965) has shown, however, that the Freundlich equation may be derived by combining an expression for the free energy of the surface with the Gibbs adsorption equation. But this derivation holds only for dilute solutions where $x/m = \Gamma_2$, the surface excess. The final result is an equation which is converted into the Freundlich equation if a term $\frac{RT(x/m)m}{\sigma_1 - \sigma_2}$ is equated with $1/n$, where σ_1 and σ_2 are the free surface energies when the surface is in contact with pure solvent and pure solute, respectively, $(x/m)_m$ is the maximum monolayer capacity for the solute per gram of adsorbent, T is the absolute temperature, and R the universal gas constant.

In addition to the constant k obtained when log x/m is plotted against log c, another constant we may designate as k' is obtained when log x/m is plotted against log (c/c_o). The k and k' values serve as indices of adsorption. They equal the hypothetical x/m values for a constant c or c/c_o value--c and c/c_o equaling unity in the case of k and k', respectively. The usefulness of the k' values lies in the assumption that while the curves relating fugacity and concentration may vary widely with temperature, solvent, or the isomer used as solute, those relating fugacity and reduced concentration will tend to group closely together or form a single curve. This implies the assumption that it is the position of a particular solute concentration relative to the saturated solubility, which is the factor determining the solute's fugacity in the solvent. The k' values may, consequently, be considered as the hypothetical amount adsorbed from solutions having a nearly constant equilibrium solute fugacity. Since fugacity of the solute in the bulk phase (and therefore in the adsorbed phase) may thus be considered to be essentially constant, discussion of k' values rules out any consideration of the influence of differing solute fugacities in the bulk phase on adsorption.

Graphs of $\frac{c}{x/m}$ versus c, according to the Langmuir adsorption equation, in no case yielded linear plots. Plots of log x/m vs. log c for all the γ-BHC aqueous isotherms yielded linear plots (figure 7). Nearly linear log-log plots were obtained for the lower concentration range of the Staten peaty muck-hexane isotherms. The log-log plots for the β-BHC isotherms (figure 8) are essentially linear if the highest concentration point for each isotherm is ignored. Freundlich constants for the aqueous γ-BHC and β-BHC isotherms and for the γ-BHC-Staten peaty muck-hexane isotherms were determined by the least squares method. For the β-BHC isotherms, the highest concentration point was neglected in the calculation of these constants. Only the lowest five points were used to calculate the Freundlich constants in the case of the Staten peaty muck-hexane system. These constants are presented in table 1. In each case k' was determined from the calculated k and 1/n values by means of the equality $k' = kc_o^{1/n}$, which follows from the Freundlich adsorption equation if c/c_o is substituted for c. The same slope, 1/n, for the log-log plots holds regardless whether log c or log (c/c_o) is plotted on the abscissa.

With the exception of the β-BHC-bentonite-water system, the k values understandably decrease as temperature increases for each system. Similarly, the solubility-corrected intercept values, k', increase in each case as temperature increases.

It is interesting to note that, with the exception of the γ-BHC-Venado clay-water system at 10°C, the 1/n values increase uniformly for each adsorbent as temperature increases. This is predicted on the basis of the derivation of the Freundlich equation for dilute solutions given by Kipling. It was observed that by letting $\frac{RT(x/m)_m}{\sigma_1-\sigma_2}$ equal 1/n, Kipling's expression reduced to the Freundlich equation. One would, therefore, except 1/n values for the isotherms of the system to relate to one another as the ratio of the corresponding absolute temperatures T_2/T_1. Table 2 shows that, with the exception of the γ-BHC-Venado clay-water system at 10° and 20°C, all the 1/n ratios are within 3.2% of the corresponding T_2/T_1 ratios. This validates the nature of the relationship between temperature and 1/n given by the above equality.

A consideration of the relationship between 1/n values and temperature leads one to conclude that normal isotherms of the same system for different temperatures will inevitably cross at some equilibrium concentration point since they tend to converge in the lower concentration range. This is strictly true only if the same 1/n values apply to the entire concentration range studied. Thus, the crossing (at about 24 μg/ml equilibrium concentration) of the 10°C and 20°C isotherms for the γ-BHC-Staten peaty muck-hexane system (figure 5a) can be explained on this basis. In the corrected isotherms, since the relative position of the isotherms for a given system is in general completely reversed from that in ordinary isotherms, corrected isotherms would be expected never to cross, but to diverge throughout the entire concentration range. This is illustrated in figure 5b.

With the exception of the silica gel-water systems, table 1 shows higher k values for β-BHC than for γ-BHC. The smaller k values on silica gel for β-BHC compared to γ-BHC may be discussed in relation to the k values for the bentonite-water systems. It appears that because of the zero dipole moment of β-BHC and the consequent absence of any dipole-dipole type interaction as an adsorptive force, the net adsorptive forces between β-BHC molecules and the adsorbents silica gel and Ca-bentonite are less than those for γ-BHC molecules. The reason why k values for β-BHC decreased with silica gel but increased somewhat with Ca-bentonite relative to γ-BHC may be related to spacial or geometric factors. It may be that once β-BHC molecules are adsorbed between clay layers and possibly between the saturating cations on the oxygen surface of Ca-bentonite, their displacement by water molecules is more difficult than such displacement on the relatively 'unprotected' oxygen surface of silica gel. Thus, even though a higher solution fugacity of β-BHC (compared to γ-BHC) provides a greater driving force toward adsorption, the relative ease energetically with which water molecules can displace these β-BHC molecules on most sites on silica gel because of the dipole moment of the former, results in k values lower than those obtained for γ-BHC. The higher k values of β-BHC compared to γ-BHC for the other three adsorbents is probably due primarily to the lower solubility limit of β-BHC and its consequent higher fugacity in solution than γ-BHC at equal concentrations.

As seen in table 1, values of k' increase with temperature for each system. Even in the cases where no clear difference between the two corrected isotherms could be observed on the graphs, as with the silica gel-water systems, a definite small increase in k' is seen to result from the temperature increase. Since the solute fugacity is considered to be constant here, temperature may have effected such increases through its influence upon fugacity of the solvent molecules adsorbed on the surface. Comparison of k' values for the γ-BHC-hexane and γ-BHC-water systems containing Ca-Staten peaty muck reveal that the γ-BHC molecule actually competes more effectively with hexane molecules than with water molecules on this adsorbent. This would lead one to conclude that the polar character of γ-BHC may be as important on this adsorbent as we have already assumed to be true on the crystalline adsorbents. It is likely that γ-BHC competes most effectively with hexane for sites on the mineral portion of this soil. Uniformly lower k' values were obtained for β-BHC compared to γ-BHC adsorption from water for corresponding adsorbents. The reason for this would appear to lie in the non-polar character of the β-BHC molecule, and the consequent reduction of ability to compete with water molecules. The lowest k' values (for β-BHC on silica gel) may be explained as was done above in the discussion of the k values.

In the following and final article of this series, the differential heats of adsorption applied to these isotherm adsorption studies will be presented and discussed.

SUMMARY

Linear normal isotherms (x/m vs. c) and 'corrected' isotherms (x/m vs. c/c_0) were obtained for adsorption of 1,2,3,4,5 and 6-hexachlorocyclohexane on four materials from water and hexane. Comparing these two types of isotherms one concludes that the effect of temperature on solubility is the only factor tending to make the adsorption process in these systems exothermic. With one exception, the relative positions of the aqueous γ-BHC and β-BHC isotherms with respect to the four adsorbents were the same. Linear log-log plots were obtained for the aqueous γ-BHC and β-BHC systems and for the lower concentration range of the γ-BHC-Staten peaty muck-hexane system. The Freundlich constants k and 1/n were calculated, as well as k', which is comparable to k when log x/m is plotted against log (c/c_0). The constants 1/n for each system were observed to increase with temperature according to the theory for dilute solutions. Given this fact, it is inevitable that the normal isotherms for a given system will cross, but corrected isotherms will diverge throughout,

provided 1/n values remain constant over the entire concentration range. Values of k' may be considered to represent hypothetical x/m values at nearly constant solute fugacities. With the exception of the silica gel-water systems, higher k values were obtained for aqueous β-BHC adsorption than for γ-BHC. The k' values were always lower for β-BHC adsorption from water than for γ-BHC adsorption. The higher k values were, thus, considered to be completely due to the lower solubility of β-BHC in water. When the solubility effect is removed, the adsorbability of γ-BHC is seen to be greater, quite possibly because it, unlike β-BHC, possesses a dipole moment. Higher k' values were obtained for the adsorption of γ-BHC on Staten peaty muck from hexane than from water. One may conclude that at constant solution fugacities γ-BHC competes somewhat more effectively on this soil with hexane than with water. In the case of the hexane solutions adsorption of lindane probably occurs on the inorganic fraction while in aqueous solutions it would probably be adsorbed on the organic fraction.

Table 1. Freundlich Constants for the Isotherms

Isomer and Solvent	Adsorbent	T (°C)	k	k'	1/n	n
aqueous γ-BHC	Ca-Staten peaty muck	10	377		.956	1.046
		20	331	2630	.969	1.032
		30	269	3350	.981	1.020
		40	197		.983	1.017
	Ca-Venado clay	10	53.8		.866	1.155
		20	45.7	277	.841	1.189
		30	41.3	363	.845	1.183
		40	36.1		.846	1.181
	Ca-bentonite	20	2.92	19.5	.886	1.128
		30	2.71	28.2	.911	1.098
	Silica gel	20	6.88	51.2	.938	1.065
		30	4.62	54.2	.957	1.045
γ-BHC in hexane	Ca-Staten peaty muck	10	0.974	3340	.886	1.128
		20	0.823	6180	.935	1.070
aqueous δ-BHC	Ca-Staten peaty muck	20	456	1170	.950	1.053
		30	437	1550	.990	1.010
	Ca-Venado clay	20	62.8	148	.861	1.162
		30	60.2	187	.883	1.132
	Ca-bentonite	19.8	3.96	9.33	.863	1.158
		30	4.46	13.9	.885	1.130
	Silica gel	19.8	2.13	5.60	.971	1.029
		30	1.64	5.80	.985	1.015

Table 2. Relation between Freundlich 1/n values and temperature

Isomer and Solvent	T_2 (°C)	T_1 (°C)	T_2/T_1 (°K/°K)	$(1/n)_{T2}$ / $(1/n)_{T_1}$ where $T_2 > T_1$			
				Staten	Venado	Bentonite	Silica gel
aqueous γ-BHC	20	10	1.035	1.013	.972		
	30	20	1.034	1.012	1.005	1.028	1.020
	40	30	1.033	1.002	1.002		
γ-BHC in hexane	20	10	1.035	1.055			
aqueous β-BHC	30	20	1.034	1.042	1.026	1.025	1.014

Literature Cited

Edwards, C. A. Insecticide residues in soils. Residue Reviews 13:83-132, 1966.

Faust, S. D. and I. H. Suffet. Recovery separation and identification of organic pesticides from natural and potable waters. Residue Reviews 15:44-116, 1966.

Gargantini, H., O. Gianotti, and R. DeTella. Leaching of BHC (gamma isomer) from Bauru sandy soil. Bragantia 16:73-79, 1959. Soils and Fertilizers 22 (3), 1343, 1959.

Kipling, J. J. Adsorption from Solutions of non-electrolytes. Academic Press, 1965.

Lichtenstein, E. P. Movement of insecticides in soils under leaching and non-leaching conditions. J. Econ. Ent. 51:380-383, 1958.

Lind, E. L., M. E. Hobbs, and P. M. Gross. The electric moments of five of the isomeric hexachlorocyclohexanes. J. Am. Chem. Soc. 72:4474-77, 1950.

Mills, A. C. The adsorption of the gamma and beta-isomers of 1,2,3,4,5,6-hexachlorocyclohexane on soils. Ph.D. thesis, University of California, Davis, 1967.

Shepard, H. The chemistry and action of insecticides. McGraw-Hill Book Co., 1951.

Swanson, C. L. W., F. C. Thorp, and R. B. Friend. Adsorption of lindane by soils. Soil Science 78:379-388, 1954.

Literature Cited

Barrow, Gordon M., Physical Chemistry, McGraw-Hill Book Co., Inc., (1961).

Bower, C. and Gschwend, F., *Soil Science Society of America Proceedings* 16, 342-345 (1952).

Edwards, C. A., Residue Reviews 13, 83-132 (1966).

Faust, S. D. and Suffet, I. H., Residue Reviews 15, 44-116 (1966).

Lichtenstein, E. P., *Journal of Economic Entomology* 51, 380-383 (1958).

Lind, E. L., Hobbs, M. E., and Gross, P. M., *Journal of the American Chemical Society* 72, 4474-77 (1950).

Nose, K., Suzuki, T., and Fukunaga, K., Pentachlorophenol (PCP) adsorption on soil. (Part 2), *Soil Science and Plant Nutrition* 10(2), 45 (1964).

Odumanova-Dunaeva, G. A., and Kozlova, K. I., *Botan*. *Zh*. 49(9), 1272-78 (1964).

Press, J. M., *Bulletin of the World Health Organization* 20, 153-162 (1959).

Swanson, C. L. W., Thorp, F. C., and Friend, R. B., *Soil Science* 78, 379-388 (1954).

Verwey and Overbeek, *Theory of the Stability of Lyophobic Colloids*, Amsterdam. (1948).